

THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

Services Technical Information Agency

our limited supply, you are requested to return this copy WHEN IT HAS SERVED USE so that it may be made available to other requesters. Your cooperation is appreciated.

46161

GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO LIABILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT HAS FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY ANY OTHER PARTY OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PARTY TO MANUFACTURE, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, OR TO PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

Reproduced by
DOCUMENT SERVICE CENTER
NOTT BUILDING, DAYTON, 2, OHIO

CLASSIFIED

46161

1946

ACTED COPY

**ULTRASONIC AND ELECTROCHEMISTRY
RESEARCH LABORATORY**

Department of Chemistry
WESTERN RESERVE UNIVERSITY
Cleveland, Ohio

ULTRASONICS AND ELECTROCHEMISTRY

THE OXYGEN ELECTRODE

by

R. R. Witherspoon, Herman Urbach, Ernest Yeager
and Frank Hovorka

Technical Report No. 4

1 October 1954

Office of Naval Research
Contract No. Nonr 561(00)
Project No. NR 359-277

Electrochemistry Research Laboratory
Department of Chemistry
Western Reserve University
Cleveland, Ohio

BEST AVAILABLE COPY

	<u>Page</u>
List of Figures	11
Abstract	1v
Preface	vi
Part I: Historical Background	1
A. Thermodynamic Considerations	1
B. Characteristics of the Static Oxygen Electrode	6
C. The Dynamic Electrode	11
Part II: Experimental Procedures for the Study of the Oxygen Electrode	24
A. Methods	24
B. The Measurement of Polarization	25
C. The Measurement of Cathode Efficiency	45
Part III: Experimental Results	47
A. Static Measurements	47
B. Dynamic Measurements	48
Part IV: Discussion of Experimental Results	81
A. The Overall Electrode Reaction	81
B. The Mechanisms of the Reaction	89
C. The Role of the Electrode Surface	92
D. Catalytic Decomposition of Peroxide	96
E. Theoretical Considerations of Polarization	103
F. The Oxygen Electrode in Acid and Neutral Solu- tions	130
G. Future Work	133
Bibliography	136
Distribution of Report	138

LIST OF FIGURES

Figure	Page
1. Free Energy-Oxidation State Relationships of the Oxygen System in Acid Solution at 25° C.	2
2. Free Energy-Oxidation State Relationships of the Oxygen System in Basic Solution at 25° C.	3
3. E.M.F. vs. H_2O_2 Concentration	3
4. Potential of the O_2 Electrode in 2 N H_2SO_4 vs. Oxygen Pressure	9
5. Current-Voltage Curves for Various Temperatures	9
6. Polarization Curves for the Cell: Porous carbon, O_2 /electrolyte/Zn or Pt porous carbon	21
7. Current-Voltage Curves for Various Active Carbons ..	21
8. General Form of Apparatus	27
9. Electronic Commutator: Block Diagram	30
10. Block Diagram of Commutator, Cell, and Detector	32
11. Detail of Electrode Placement in Cell	33
12. Detail of the Electrode	36
13. An Electrode for Static Measurements	37
14. Detail of the Efficiency Cell and Circuit	46
15. Effect of Peroxide Concentration on Static Potential	49
16. Polarization of Air Cell and Sprayed Electrodes	51
17. Effect of Peroxide Concentration on Potential at Low Current Density	52
18. Comparison of Binding Materials	53
19. Time Dependence of Bonded Carbon Electrodes at Constant Current Density	55

Figure	Page
20. Polarization of Various Carbons	57
21. The Effect of KOH Concentration on Polarization	59
22. Dependence of Potential on KOH Concentration	60
23. Polarization in NaOH and KOH	61
24. Polarization in Various Alkalies	62
25. Polarization at Constant Ionic Strength	64
26. Potential-Current Relationships in Neutral and Acid Electrolytes	65
27. Effect of Increased Peroxide Concentration on Polarization	66
28. The Effect of Peroxide Concentration on Polarization at Constant Current Density	67
29. The Effect of Peroxide Concentration on Polarization at Constant Current Density	68
30. Polarization at High and Low Peroxide Concentration	70
31. Polarization at High Peroxide Concentration	71
32. Effect of Oxygen Partial Pressure on Polarization ..	72
33. Oscilloscope Decay Traces	74
34. Polarization of Silvered Carbon	76
35. Performance of Impregnated Active Carbon	76a
36. Comparison of Electrolytes for Silver Treated Carbon	78
37. Polarization of an Electrodeposited Silver Electrode	80
38. Curves of the Components of Concentration Polariza- tion	113
39. Equivalent Electrical Analogue in the Resistivity Effect	120
40. Potential vs. pH Curve	129

THE OXYGEN ELECTRODE

Technical Report No. 4

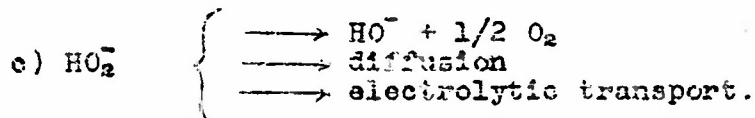
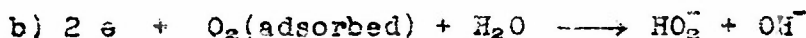
by

R. R. Witherspoon, Herman Urbach, Ernest Yeager
and Frank Hovorka

- Abstract -

The kinetics of the oxygen electrode have been studied on carbon surfaces by means of cathodic polarization measurements. The polarization has been determined by the indirect method with electronic instrumentation. The characteristics of the oxygen electrode have been obtained as a function of the type of carbon surface, the nature of the electrolyte, ionic strength, pH, peroxide concentration, temperature, oxygen pressure, current density, time, and catalysts included with the carbon. On the basis of these measurements, the following conclusions have been reached concerning the oxygen electrode in alkaline solution:

1. The oxygen electrode with carbon proceeds according to the mechanism



2. At apparent current densities as high as 500 ma./cm², the cathodic polarization appears to be primarily the result of concentration polarization involving a) the build-up of perhydroxide ion concentration at the electrode surface, and b) the depletion of physically adsorbed oxygen at the sites of the electrochemical reaction.

3. The electrochemical step (b) seems to be reversible even at apparent current densities greater than 100 ma./cm².

4. The use of a water-proofing component in the carbon electrodes is necessary to prevent the solution from filling the pores and capillaries in the carbon. Transfer of oxygen to the effective sites for the electrochemical step (b) cannot take place effectively through solution-filled pores. The transfer process probably involves the surface mobility ascribed often to physically adsorbed species as well as gaseous diffusion.

5. The concentration polarization can be greatly decreased through the increase of the oxygen pressure and the inclusion of peroxide decomposing catalysts in the carbon or the electrolytic solution.

6. The electrochemical reduction of the perhydroxide ion does not take place to any appreciable extent with any combination of particular types of carbons and catalysts examined as of date. The electrochemical formation of the HO₂⁻ ion is characterized by a low energy of activation because the oxygen-oxygen bond is not broken. This is not true of the further reduction of HO₂⁻, however.

7. Carbon electrodes deteriorate more rapidly at current densities above 50 ma./cm² in sodium hydroxide than potassium hydroxide unless peroxide decomposing catalysts are included in the carbon. The formation of sodium peroxide in the pores of the carbon is believed to be responsible for this difference in performance in the two electrolytes.

8. The oxygen cathode is capable of operating on pure oxygen gas (1 atm.) at current densities in excess of 150 ma./cm² for weeks at a time with polarization less than 0.15 volts.

This report also contains a brief survey of the literature relating to the oxygen electrode. In addition, the concentration polarization at an oxygen electrode has been considered theoretically. The mathematical results compare favorably with the experimentally determined polarization data.

- Preface -

In Technical Report No. 2 the results of preliminary measurements with the oxygen electrode were described. Since the preparation of this earlier report in 1953, the investigation of the oxygen electrode has proceeded considerably further, and the oxygen electrode is now more fully understood with respect to its performance in alkaline solutions. This more recent work is described in the present report.

Much of this report is based on the theses submitted by two of the authors (R. R. Witherspoon and E. B. Urbach) in partial fulfillment of the requirements for the Ph.D. degree in the Department of Chemistry at Western Reserve University.

THE OXYGEN ELECTRODE

Part 1. Previous Work on the Oxygen Electrode and Related Systems

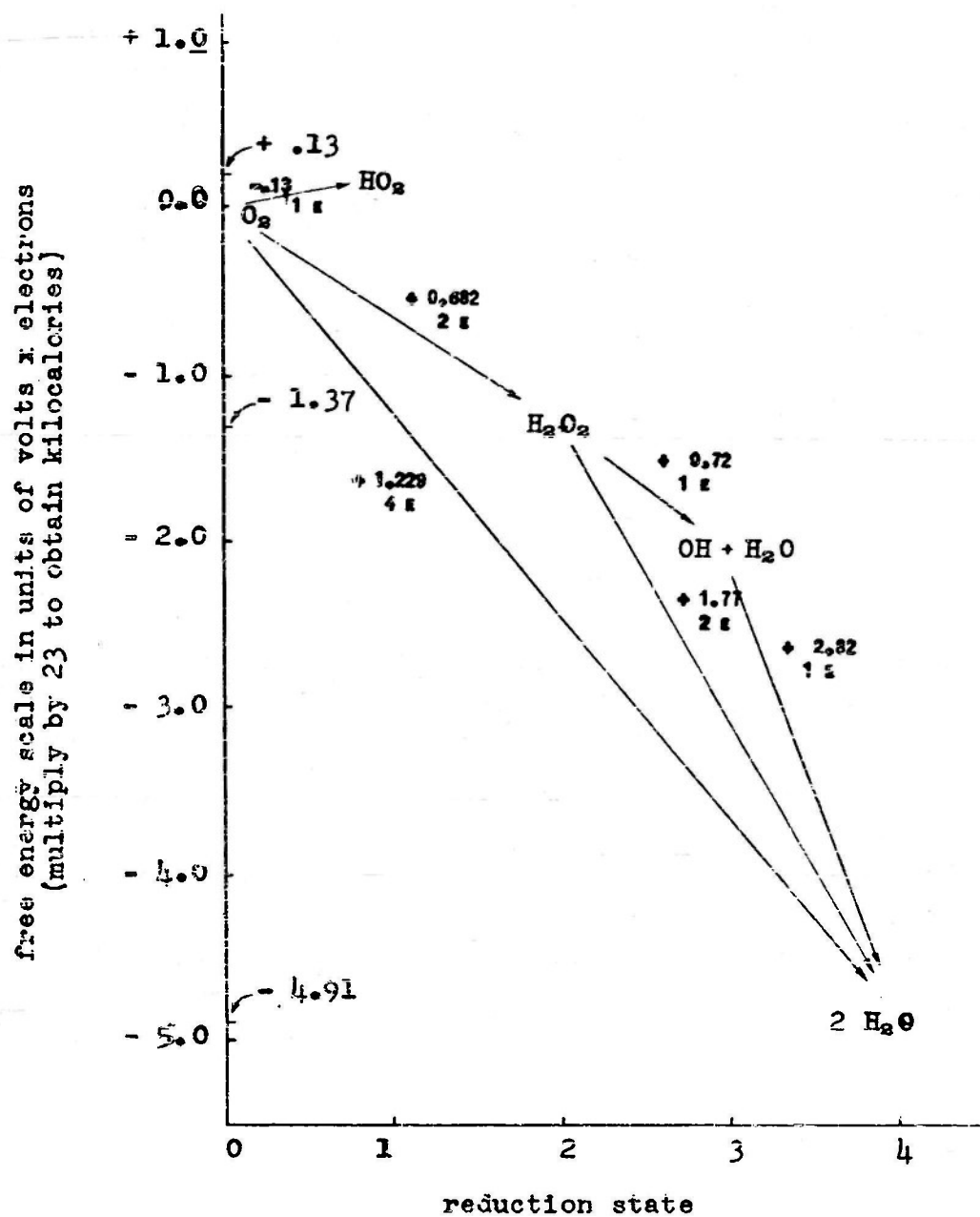
The literature survey which follows will be considered under the topics of thermodynamics, static behavior, and dynamic behavior.

A. Thermodynamic Considerations

Theoretically any system of inert conductor and electrolyte may be considered an oxygen electrode if molecular oxygen is directly or indirectly involved in the electrochemical process occurring at the electrode-electrolyte interface. Therefore, a prerequisite of any study in this field is a knowledge of the precise electrochemical reactions and the theoretical potentials associated with oxygen.

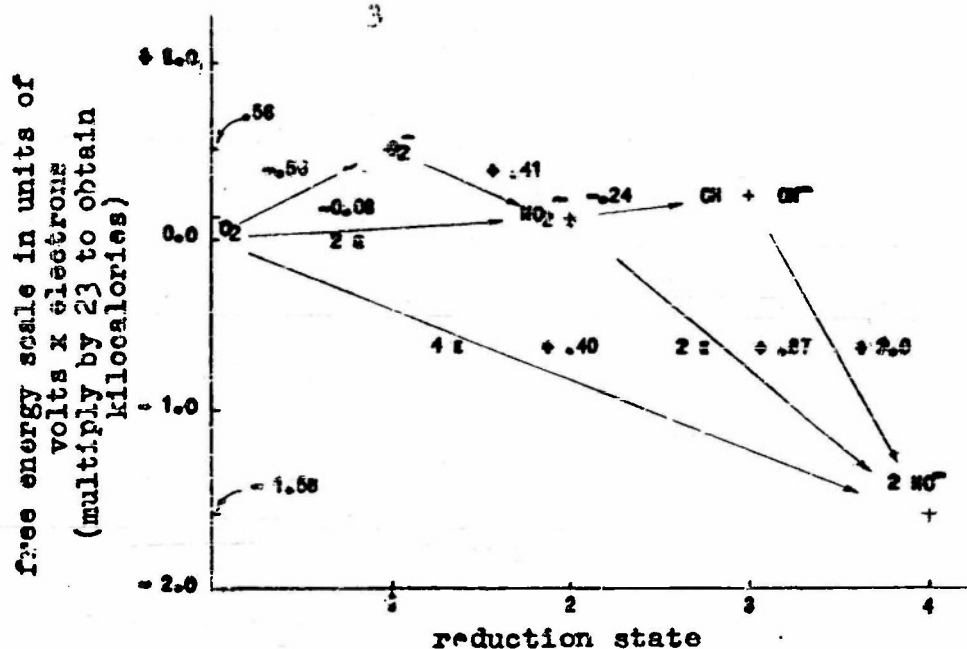
The free energy oxidation state relationships of the oxygen system have been graphically illustrated in Figures 1 and 2 from the tabulation of Latimer.¹ Of note is the fact that the theoretically available free energy resulting from the total electrochemical reduction is threefold greater in acid than it is in basic solution.

¹W.M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Second Edition, Prentice Hall Co., New York, 1952, p. 50.



Free Energy - Oxidation State Relationships of
the Oxygen System in Acid Solution at 25° C

Figure 1



Free Energy-Oxidation State Relationships
of the Oxygen System in Basic Solution at 25° C.

Figure 2

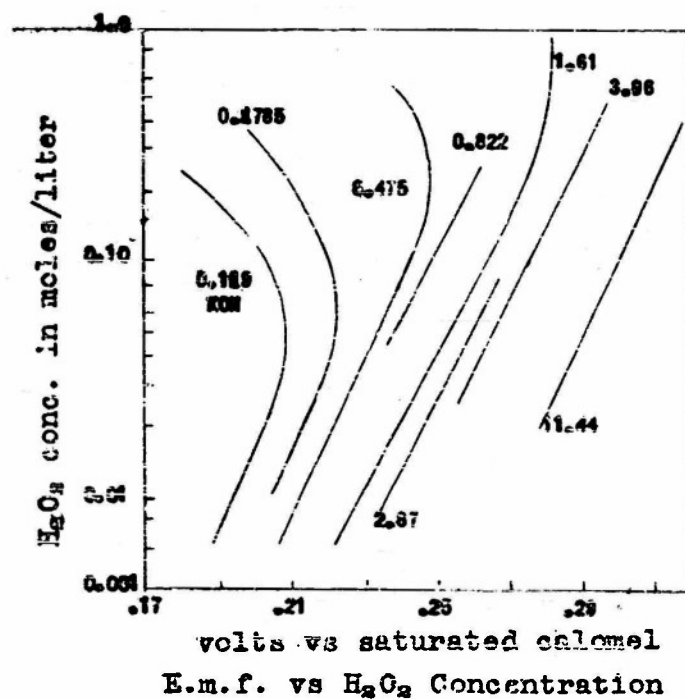
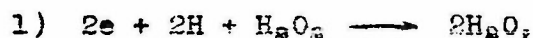


Figure 3

In practice, multiple electron transfer processes generally occur in a series of steps because of the large activation energy required to go from one state to another. Of all the possible modes of reaction originating with relatively stable molecules or ions,^{2,3} the literature indicates only two appear to have sufficient velocity to warrant their study as possible sources of electrochemical energy and as reversible electrodes. These are



i.e., peroxide reduction to water in acid media and



i.e., oxygen reduction to peroxide in basic media.

The reaction involving the formation of superoxides is also fast. In view of the rapid conversion of superoxides to peroxides in the presence of water, the overall process is equivalent to reaction (2), which will be the primary concern of this report.

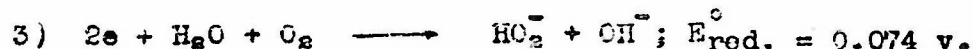
Considerable evidence, to be presented later, indicates that the reduction of oxygen to peroxide can occur under relatively reversible conditions in alkaline solution.

² Yeager, Witherspoon, Urbach, and Hovorka, Technical Report No. 2, Office of Naval Research, Contract No. N onr 581 (00) Project No. NR 354-277 (1952).

³ Weisz and Jaffe, Trans. Electrochem. Soc., 93, 128 (1948).

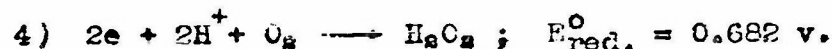
5

Lewis and Randall⁴ calculated the standard e.m.f. of the oxygen-peroxide couple in basic solution as follows



where E represents the standard potential of the oxygen-peroxide couple at unit activity of base and peroxide.

The potential of the hydrogen peroxide couple at unit activity of hydrogen ion is expressed by the equation



These theoretical data have served to establish the empirical validity of the measurements of Bornemann⁵, who had previously obtained a value of $0.63 \pm .03$ volts with an oxygen-platinum electrode in acidic peroxide solutions. This value is in agreement with the Lewis and Randall value of 0.682 volts. W.G. Berl's⁶ extensive measurements with oxygen activated carbon electrodes in basic solution yielded the empirical value -0.042 volt which must be compared with the -0.074 volt calculated by Lewis and Randall. The discrepancy between the two values (1290 calories) is small if one considers the accuracy of most thermal data and the fact that the

⁴Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Co., New York, 1923, p. 475.

⁵K. Bornemann, "Nernst Festschrift," Knapp, Halle, 1912, p. 118.

⁶W.G. Berl, Trans. Electrochem. Soc., 63, 253 (1943).

theoretical value is a relatively small value derived from the algebraic sum of large numbers. Furthermore, the empirical value itself requires assumptions regarding the junction potential and the activity coefficients of the perhydroxide ions.

B. The Characteristics of the Static Oxygen Electrode

1. Peroxide and Hydroxide Ion Effects

The static potential of the oxygen electrode should follow the Nernst equation. This can be ascertained in terms of the dependence of the potential on the oxygen pressure and the activities of the hydroxide and perhydroxide ions. The appropriate relationship originates from equation (3) which is associated with the oxygen-peroxide half cell, i.e.

$$5) E = E^{\circ} - \frac{RT}{nF} \ln \frac{(a_{OH^-})(a_{HO_2^-})}{(P_{O_2})}$$

The a_{OH^-} and $a_{HO_2^-}$ represent the activities of the species in the subscripts and the pressure of oxygen is P_{O_2} , R is the gas constant, F the faraday, T the absolute temperature, and n the number of electrons. The data of W.G. Berl⁶ are presented in Figure 3 and substantiate the predictions of the Nernst equation which requires a linear dependence of the potential on the logarithm of the activities of the reaction ingredients.

The electrode of Berl consisted of a porous graphite cylinder which was sprayed with a thin coat of activated

carbon in a toluene-ethanol solution of ethylcellulose. During the measurement oxygen gas was supplied to the inside of the cylinder so that the oxygen bubbles issued uniformly from the external carbon layer.

2. Oxygen Pressure Effects

Unfortunately no reliable measurements of oxygen pressure versus potential relationship exist. The data of Winslow⁷ were obtained in 2 N H₂SO₄ with an active carbon electrode. No fixed amount of peroxide was added, and no effort was made to measure the peroxide produced by transients. The curve (Figure 4) vaguely resembles a logarithmic plot.

The break in the curve at 745 mm. of Hg is the subject of speculation by the author but does not warrant too serious consideration until experiments with adequate peroxide controls yield similar reproducible results. Kordesch and Martinola⁸ studied the potential changes produced in the cell

O₂, carbon/electrolyte/Zn

with air (oxygen pressure 0.21 atm.) and subsequently with a mixture of 99% nitrogen and 1% oxygen. They too appear to have neglected a peroxide control. Their measurements required hours for stabilization. They

⁷ N.M. Winslow, Trans. Electrochem. Soc., 92, 411 (1947).

⁸ Kordesch and Martinola, Monatsch., 84, 39 (1953).

reported a potential change of 0.038 volt in 6 N KOH for the 20-fold variation in oxygen pressure. This is in agreement with the 38 mv. calculated from the Nernst equation. In solutions less alkaline, however, smaller changes in the potential indicated a less sensitive response to the changes in the oxygen partial pressure. At pH below 9 in the acid range a 20-fold difference in the oxygen partial pressure produced a change of only 4 mv. or less in the potential.

3. Temperature Effects

In Figure 5 are illustrated graphically the thermal behavior of the oxygen electrode. Bratzler⁹ reported a temperature coefficient of 3 mv./°C in KOH without a peroxide control.

The temperature coefficient of the oxygen electrode in 1 M KOH was measured in the cell

O₂, carbon/ 1 M KOH/Zn

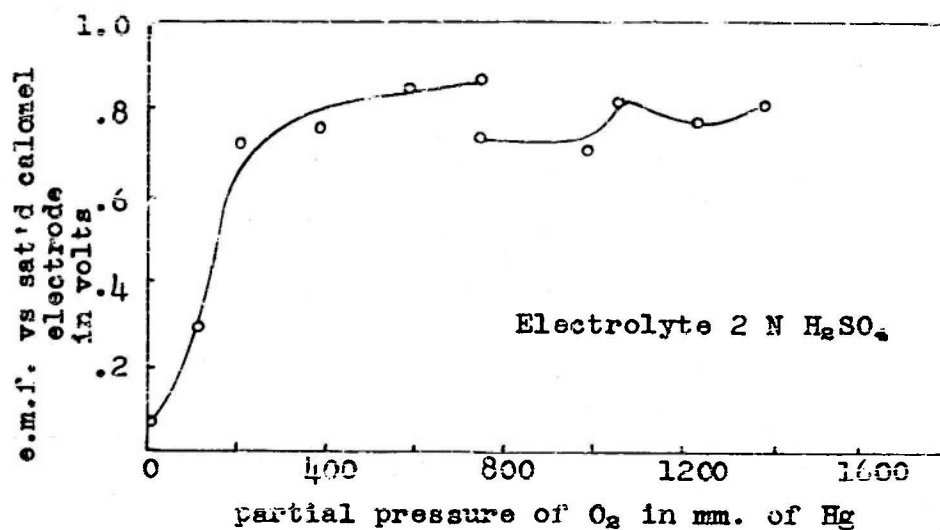
without a peroxide control by Kordes and Martinola.⁸

By subtracting the temperature coefficient of the zinc half cell they obtained a value of -7.4×10^{-4} v./°C.

4. Static Measurements With Metallic Electrodes

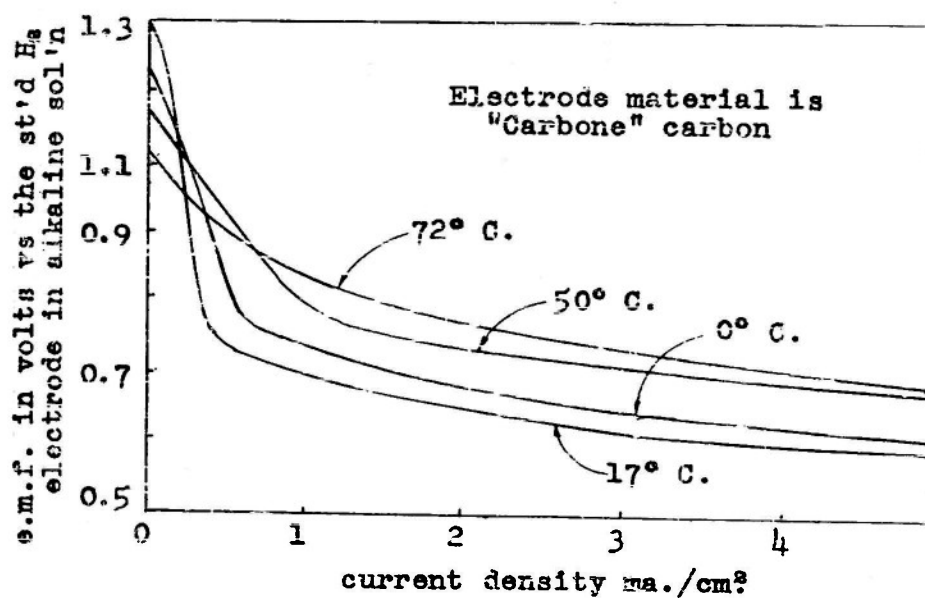
Thus far the discussion has been limited to oxygen electrodes constructed of carbon in some form as the inert electrode material. Theoretically any passive conducting

⁹ K. Bratzler, Z. Elektrochem., 54, 81 (1950).



Potential of the O_2 Electrode in 2 N H_2SO_4
versus Oxygen Pressure⁷

Figure 4



Current-Voltage Curves for Various Temperatures⁹

Figure 5

material might act as an oxygen electrode. In practice the degree of reproducibility obtained with metallic electrodes has been disappointing. The work of Bain¹⁰ with the noble metals indicates that greatest reproducibility is obtained only in basic solutions where values for the various metals most nearly approximate one another. The time period required for attainment of the limiting equilibrium values were of the order of weeks. Since these values were subject to the same experimental restrictions as the data of Winslow,⁷ relatively little thermodynamic significance may be ascribed to them.

Weisz and Jaffe³ tested electrodes of sintered silver and nickel using known concentrations of peroxide in KOH. The silver showed a response of 0.043 volt for a tenfold change in the concentration of the peroxide while the nickel was insensitive and showed no change in potential with changing peroxide concentration. These values may be compared with the calculated value of 0.039 volt and the experimental value of 0.034 volt obtained with an active carbon electrode.

Dynamic checks of the static reversible values for metals at pH of 7 and 1 were obtained by Hickling and Wilson¹¹ from polarographic half wave potentials. In neutral solutions the theoretical value plus their

¹⁰ H.G. Bain, Trans. Electrochem. Soc., 78, 183 (1940).

IR drop was 0.42 volt which compares with the observed average of 0.48 volt for platinum, gold, nickel, and graphite microelectrodes. In acid solution the observed average was 0.80 volt compared to the theoretical values of 0.79 volt. The most divergent values were obtained with metals which were good peroxide catalysts. This indicated a sensitivity to the presence of peroxide by nickel and other metals not found by Weiss and Jaffe.

C. The Dynamic Electrode

1. Anodic behavior

a. Oxidation of peroxide. --The anodic oxidation of hydrogen peroxide on platinum, gold, nickel, and graphite microelectrodes was studied by Hickling and Wilson¹¹ in alkaline, neutral, and acid solution. The current efficiency was determined by measuring the amounts of oxygen produced per quantity of charge. The correction for the catalytic decomposition of the peroxide was neglected. If this error is not considered, it would appear that at all pH ranges, providing the current density is not excessive, peroxide is quantitatively reduced to an oxygen molecule for two faradays of charge.

b. Concentration effects. --Hickling and Wilson found that the half wave potential increases almost

¹¹ Hickling and Wilson, J. Electrochem. Soc.,
98, 425 (1951).

linearly with the pH. Increasing peroxide increases the half wave potential in an irregular fashion at all pH ranges with the exception of platinized platinum microelectrodes in acid solution.

2. Cathodic Behavior

a. Experimental and practical cell types. -- A

brief summary of some cells which have appeared in the literature is presented here with some mention of current-voltage characteristics at the risk of later repetition before formal current efficiency and polarization data are discussed. Most of these data will be unsatisfactory for quantitative interpretations since they represent the sum total of anodic polarization, and IR drop in the electrodes and electrolyte as well as cathodic polarization.

¹²Martin van Marum noted that Volta's pile was more energetic when placed in an oxygen atmosphere. Biot and Cuvier¹³ discovered gas adsorption by the pile and increasing polarization upon depletion of the gaseous supply. Adie¹⁴ observed that aerated water activated a platinum-zinc couple.

¹²M. van Marum, Ann. Chim., 41, 77 (1801).

¹³Biot and Cuvier, Ann. Chim., 39, 242 (1801).

¹⁴R. Adie, Phil. Mag., 31, 350 (1847).

The rekknowned Grove cell¹⁵ was simply a sulphuric acid solution with platinum electrodes in contact with hydrogen and oxygen. Leclanche¹⁶ obtained an improved output from his manganese dioxide cell by exposing the upper part of the MnO_2 carbon mix, only partially wetted by the electrolyte, to the atmosphere. L. Maiche¹⁷ (1879) attempted to fabricate a true air depolarized cell by replacing the manganese dioxide with platinized carbon. This mix was exposed to the atmosphere.

An improvement on the Grove cell was effected by Mond and Langer¹⁸ by passing a mixture of steam and oxygen, and steam and hydrogen respectively, over perforated platinum black coated electrodes. Table 1 presents polarization data of these and other workers.

Hofmann¹⁹ contrived a cell of copper electrodes in KOH employing carbon monoxide as the anodic material and oxygen as the depolarizer. The combined cell

¹⁵ W.R. Grove, Phil. Mag., III, 14, 127 (1839).

¹⁶ G. Leclanche, Les Mondes, 16, 532 (1868).

¹⁷ L. Maiche, as quoted in "Primary Batteries" by G.W. Vinal. John Wiley and Sons, New York (1950), p. 216.

¹⁸ Mond and Langer, Proc. Roy. Soc. (London), 46, 296 (1889).

¹⁹ A.A. Hofmann, Ber., 51, 1526 (1918).

Table 1

CURRENT DENSITY POLARIZATION DATA FOR EXPERIMENTAL
AND COMMERCIAL OXYGEN DEPOLARIZED CELLS

Authors & Reference	$E_{\text{red.}} (O_2)$ volts	Ma./cm ²	Electrolyte	Polarization Volts	Electrode Material
Mord & Langer ¹⁸		7.	H ₂ SO ₄	high	Platinized Pt.
Hoffmann ¹⁹	0.20	0.8	KOH	0.72	CuO, O ₂ /Cl, CO
St. V. Naray-Szabo ²⁰	See Fig. 6	15.	15% KOH	0.55 (point of max. output)	Platinized porous C/Zn
St. V. Naray-Szabo ²⁰		16.	27% NH ₄ Cl	Same	"Le Carbon," C/Zn
Lamb & Elder ²¹	0.659	21.5	H ₂ SO ₄ & FeSO ₄	.053	Pt., C
Tobler ²²		2.78 ma./g.	Alkaline	low	4% Platinized graphite
Spiridinow ²³		20-30 low T 100 high T	Alkaline		Carbon & catalysts
Heise, Schumacher & Fischer ²⁴		7.2	NaOH	low	Active carbon/Zn

Table 1 (cont.)

Authors & Reference	$E_{red. (O_2)}$ volts	Ma./cm ²	Electrolyte	Polarization volts	Electrode Material
W. G. Berl ⁶		150	5M KOH	below .25	Active C
Weisz & Jaffe ³	1.45	25	5M KOH	.02	Active C
Bratzler ⁹	See Fig. 5	115 ma./g.	Alkaline	-.35	Active C
Marko & Kordezh ²⁵		20-30	Alkali	low	Active C

polarization was 0.72 volt at only 0.8 ma./cm.²

Oxygen electrodes of porous and platinized porous carbon versus zinc anodes were studied by S. v. Naray-Szabo.²⁰ Oxygen was blown through the center of the electrode via the pores.

Lamb and Elder²¹ immersed a platinum electrode in an acid solution of ferrous sulphate containing a suspension of active carbon. The potential was that of the ferrous-ferric system maintained in the oxidized state by aeration with air or oxygen. Currents of 21.5 ma./cm.² at 0.053 volt polarization were obtained.

At the suggestion of E. Baur, J. Tobler²² compressed active carbon granules, previously water-proofed with paraffin, into porous plugs through which were blown air or oxygen.

By employing an active carbon membrane of thin, gas permeable material in alkaline electrolyte (vs. the hydrogen electrode), current densities of 20 to 30 ma./cm.² have been obtained at room temperature and 100 ma./cm.² at higher temperatures according to Spiridinow.²³ He constructed his electrode by pressing the active carbon upon a wire grid with rubber cement.

²⁰ St. v. Naray-Szabo, Z. Elektrochem., 33, 18 (1927).

²¹ Lamb and Elder, J. Am. Chem. Soc., 53, 162 (1931).

²² J. Tobler, Z. Elektrochem., 39, 148 (1933).

²³ P. Spiridonow, Novosti Tekhniki, 7, No. 1, 42 (1939).

Heise, Schumacher, and Fischer²⁵ developed a commercial, activated carbon-alkali zinc cell which operates successfully at 7.2 ma./cm.² with little polarization.

The electrode of W.G. Berl⁶ has been discussed. He obtained currents of 150 ma. /cm.² for short periods with little polarization using oxygen.

Special combinations of heavy metal catalysts on porous carbon electrodes were employed by Kordesch and Marko²⁵ to secure continuous currents of 30 ma./cm.² using only air. The reproducibility of their cell was applied to the determination of oxygen in gases with a sensitivity of 0.01%.

b. Reduction of oxygen to peroxide, ---Traube²⁶ has shown that at noble metal electrodes in dilute acid solution oxygen is reduced to hydrogen peroxide with a current efficiency of 100%, but that simultaneous catalytic decomposition reduces the actual yield.

The process of cathodic production of H₂O₂ devised by E. Berl²⁷ was claimed to produce dilute peroxide in alkaline solution at current efficiencies of better than

²⁴Heise, Schumacher, and Fischer, Trans. Electrochem. Soc., 92, 173 (1947).

²⁵Marko and Kordesch, Osterr. Chem. Z., 52, 125 (1951).

²⁶M. Traube, Ber., 15, 2434 (1882).

²⁷E. Berl, Trans. Electrochem. Soc., 76, 369 (1939).

90%. He stated that yields in acid solution were poor.

W.G. Berl⁶ reported that current efficiencies of 100% were obtained with an activated carbon surface sprayed on a porous graphite base for current densities up to 450 ma./cm.² in alkaline solution. This result contrasts favorably with an extremely low efficiency he obtained with graphite alone. The effect of the peroxide concentration, pH, pressure, and rate of oxygen flow on current efficiency data were not determined.

Such data have been presented in a qualitative fashion by Churchill²⁸ in the case of one metal. Formation of hydrogen peroxide by aluminum electrodes definitely appears to be a cathodic process. Two aerated electrodes of aluminum, corroding under static conditions, may produce approximately equivalent amounts of peroxide, but with the application of increasing potentials, peroxide formation is accelerated at the cathode and depressed at the anode.

The relative effects of pH are indicated in the results from aerated aluminum electrodes. In 1 and 0.2 N H_2SO_4 , 5% KCL, and K_2SO_4 peroxide was detected in large amounts, whereas in 1 and 0.1 N KOH, peroxide was not detected. With 5% KNO_3 only a faint trace resulted.

The rate of production of peroxide falls off with

²⁸J.R. Churchill, Trans. Electrochem. Soc., 76
341 (1939).

increasing peroxide according to Churchill.²⁸ It is known that the rate of decomposition is first order²⁹ in peroxide and the reduced average peroxide production is probably indicative of a decomposition rate approaching the production rate. In this connection, Weisz and Jaffe³ obtained a logarithmic curve which flattens asymptotically to a maximum peroxide concentration with time at a given current density.

In all cases, Churchill observed that an excess of oxygen was essential to the generation of peroxide. This was explained by the electrochemical reduction of peroxide at the cathode.

Weisz and Jaffe³ passed a current of 0.01 amp./cm.² through a cell containing a known peroxide concentration with graphite and mercury cathodes while permitting an identical cell to remain static as a control. After a measured amount of time, test and control were analyzed for peroxide. Though no electrochemical reduction occurred in 5 molal NaOH, in saturated NH_4Cl a considerable amount was electrochemically reduced. They noted that when aeration was simultaneously permitted to occur no peroxide was electrochemically reduced. This indicates that oxygen competes more successfully for electrons than peroxide. Thus the reaction

²⁹ Barb. Baxendale, George, and Hargrave, Trans. Far. Soc., 47, 473 (1951).



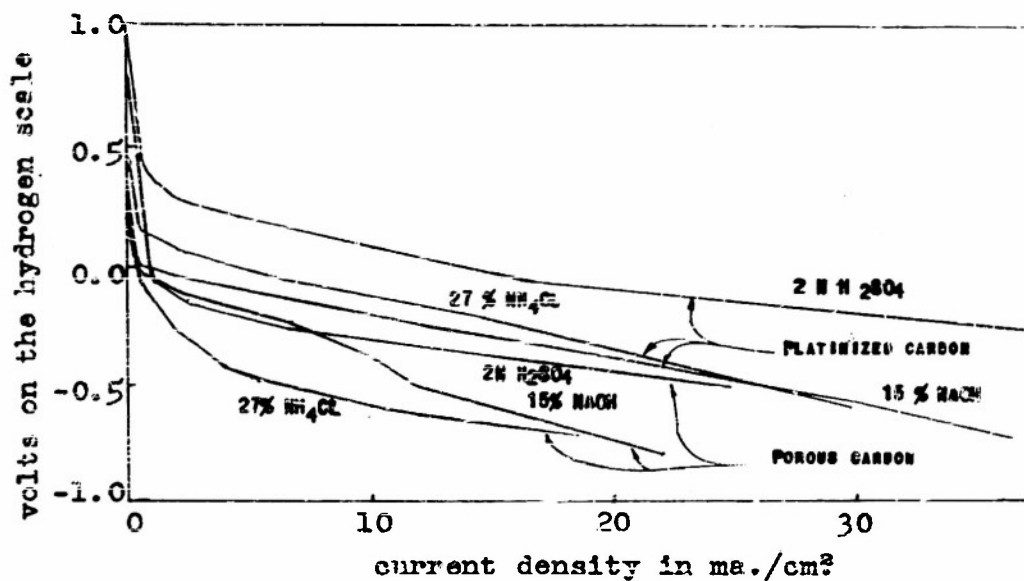
is much faster than the reaction



c. pH and cation concentration effects.--The results of St. V. Naray-Szabo²⁰ contain the IR drop within the solution, and no attempt was made to control or ascertain the concentration of perhydroxide ion. This investigator furnished qualitative data (Figure 6) on the behavior of polarization curves in solutions of varying pH. His cell was constructed of a porous platinized carbon cathode and a zinc anode with a mercurous sulphate or mercurous chloride reference electrode depending on the electrolytes. These were highly conducting solutions of 2 N H₂SO₄, 27% NH₄Cl, and 15% NaOH at pH values of 0, 3.4, and 14 respectively.

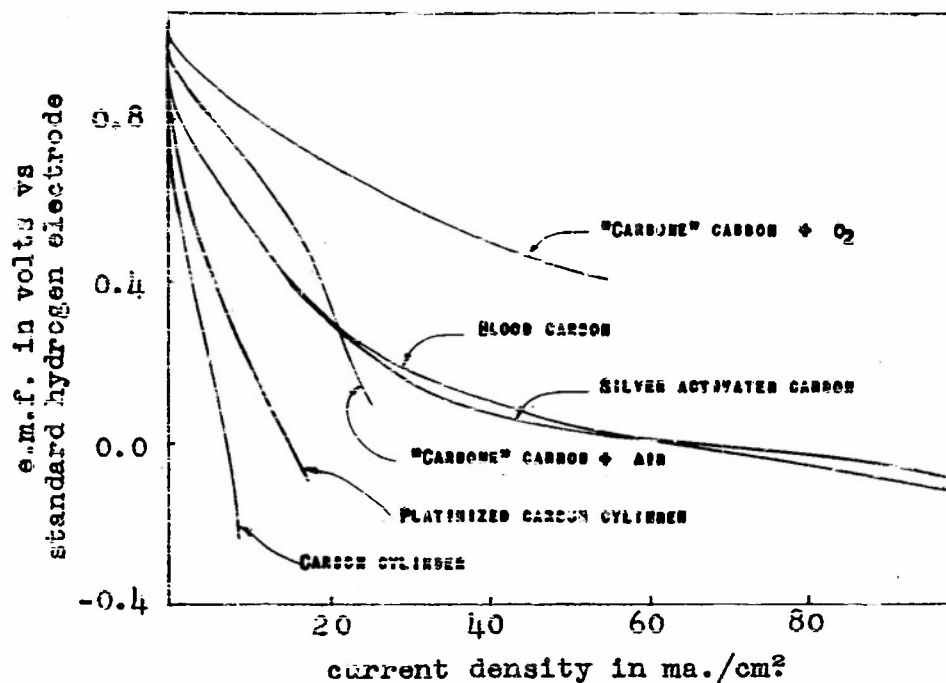
d. Catalytically activated carbon electrodes.--Polarization data for carbons activated by various processes are usually subject to the faults previously mentioned since they include IR drop and anodic polarization. In addition the measurements were generally made without adequate control of peroxide concentration, and often without control of salts derived from the solution of an active metal anode.

Figure 7 presents a comparison of catalyzed carbons used by K. Bratzler⁹. Most interesting are the "carbone" and silver activated carbons. For a comparison of platinized carbon and non-activated carbons see Figure 6.



Polarization Curves for the Cell: Porous Carbon,
 O_2 /Electrolyte/Zinc
 or Pt Porous Carbon

Figure 6



Current-Voltage Curves for Various Active Carbons⁹

Figure 7

Quite often the cathodic material is activated with a metal which (far from being passive) dissolves in the electrolyte. This has been the case with nickel and copper catalysts in strong alkalis so that it is quite possible that the catalytic action occurs in the liquid phase. The mechanisms of catalysts accelerating peroxide decomposition are described in Part V. Catalysts are usually derived from elements of variable valence. Examples are the pyrophosphate ion described by Lamb and Elder,²¹ the cuprate ion by Weisz and Jaffe,³ and iron in acid solutions with traces of copper,³⁰

e. Metallic oxygen electrodes. ---The metals tested by Tobler²² were iron, nickel, chromium, nickel, constantan, manganin, silver, and copper in the form of fine wool mesh through which was bubbled oxygen gas. In general the passive metals were such poor electrodes that it was difficult to determine whether the depolarizing action was due to the oxygen or the stirring effect of the gas bubbles. Copper and the transition metals could not be prevented from dissolving in the strong alkali. Steel and silvered copper gave optimum results.

Hofmann's¹⁹ copper-copper oxide electrode in carbon monoxide cell delivered only 0.8 ma./cm.²

M. Knobel³¹ made the suggestion that porous

³⁰ Kolthoff and Parry, J. Am. Chem. Soc., **73**, 3718 (1951).

³¹ M. Knobel, Ind. Eng. Chem., **17**, 826 (1925).

carbon electrodes be electroplated with various metals to control the overvoltage. The application of this idea to practical depolarization problems has been slight.

Metals have found employment in high temperature fuel cells with varying degrees of success. Iron coated with the oxides, silver and molten silver, lead, nickel and the platinum metals exhibited better performance than would be expected in aqueous solution at room temperature but the currents were still only 15 to 20 ma./cm.² with considerable polarization in most instances.

G. Temperature effects. --K. Bratzler's⁹ polarization curves of temperature dependence were made without a peroxide or metallic ion control (see Figure 7). He attributed the flattening of the curves at higher temperature to the fact that the peroxide concentration at the electrode is decreased by high temperature induced decomposition. A temperature coefficient of 3 mv./°C was obtained in the range of 12 to 75°C at 5 ma./cm.².

Kordosch and Martinola⁸ have studied the effects of temperature on dynamic oxygen-carbon cathodes in 1 N KOH solutions from 12 to 35°C and at a current of 5 ma./cm.². The temperature coefficient was found to be 0.5 mv./°C. Like Bratzler these workers failed to employ a peroxide control.

Part II. EXPERIMENTAL PROCEDURES FOR THE
STUDY OF THE OXYGEN ELECTRODE

A. Methods

Four methods for obtaining information about the electrode polarization are discussed below.

1. Static Measurements

Of prime necessity is a knowledge of the overall chemical reaction responsible for the electrochemical energy. The static measurements of W.G. Berl¹ were undertaken to exploit the predictions of the Nernst equation for the assumed half cell reaction. Thus the expected slope of the e.m.f. versus the activities of the participants of the reaction was obtained and substantiated the theory that oxygen is in equilibrium with the perhydroxide ion at the oxygen electrode. This technique was extended to the study of electrodes of activated carbon catalyzed with heavy metals.

2. Polarization versus Current Density

Experimentally determined relationships between current density and overvoltage may be used to verify the theoretical deductions concerning the mechanism of the process in the manner of Tafel² et al.

¹W.G. Berl, Trans. Electrochem. Soc., 83, 253 (1943).

These relationships include the additional variables of temperature, and concentration of the reactants and products.

3. Current Efficiencies

Current efficiency data yield additional information on the main electrochemical reaction and reveal the presence of possible side reactions. Moreover, they furnish information on the specific decomposition rates of peroxide under various conditions.

4. Tracer Techniques

Tracer techniques involving the use of O^{18} have been employed by Taube^{3,4} and his students to obtain information concerning the mechanisms involved in catalytic and photochemical decomposition of hydrogen peroxide. The implications of this work will be discussed later.

B. The Measurement of Polarization

1. Instrumentation

The indirect or commutator technique has been used for measuring the polarization in the present research. With this technique, the polarizing

² J. Tafel, Z. Phys. Chem., 50, 641 (1905).

³ Cahill and Taube, J. Am. Chem. Soc., 74, 2312 (1951).

⁴ Hunt and Taube, ibid., 5999.

current through the electrode is periodically interrupted for short periods during which the potential of the polarized electrode is measured relative to a reference electrode. If the potential measurement is made immediately following the interruption of the polarizing current, the voltage of the polarized electrode may be obtained without including the IR drop associated with the current. With adequate apparatus the indirect method also permits quantitative information to be obtained concerning the rate of build-up as well as decay of the polarization. In the past, many workers have objected to this method on the basis that the polarization decays an appreciable amount between the time when the current is interrupted and the time at which the potential is measured. As a result, accurate data supposedly cannot be obtained for the steady-state polarization. With recent developments in electronic instrumentation,^{5,6} the potential measurements can be made within a period of the order of 10^{-6} sec. following the interruption of the polarizing current. The amount of decay that occurs

⁵Y. Schuldiner and D. White, *J. Electrochem. Soc.*, 97, 433 (1950). D. Staicopoulos, E. Yeager, and F. Novotna, *ibid.*, 98, 68 (1951).

⁶ONR Technical Report No. 6, Ultrasonic Research Laboratory, Western Reserve University, (April, 1951), Contract No. N7 onr 47002, Project No. NR 051 162.

within one microsec. is probably negligible for all cases with the possible exception of metal electrodes which acquire passivity.

The indirect method was used for the majority of the polarization measurements in the present research because it does not impose serious physical limitations on cell or electrode design and presents more information (i.e., build-up and decay of polarization).

In Figure 8 is a diagram which partially indicates the type of information to be obtained with this apparatus. The symbols C, A, and R within the circle marked "cell"

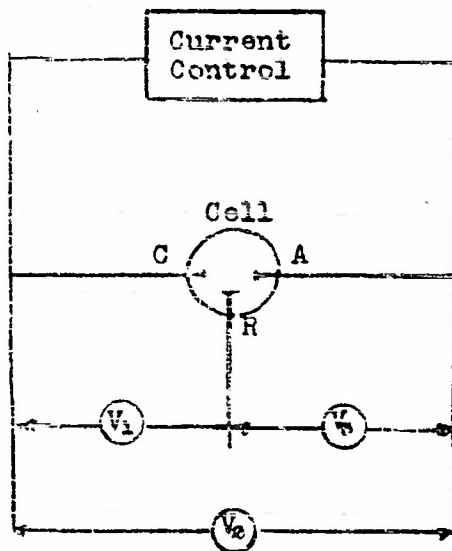


Figure 8.--General Form of Apparatus

represent the cathode, anode, and reference electrode, respectively. The block labeled "current control"

represents the apparatus for interrupting the polarizing current through the cell. The current passing through the cell is controlled by the electronic apparatus and is independent of the cell voltage or impedance. The potential may be determined between the cathode and reference (V_1), the cathode and anode (V_2), or the anode and reference (V_3) at any instant following the initiation or interruption of the polarizing current with an electronically operated potentiometer arrangement.

The general characteristics of this apparatus are summarized as follows:

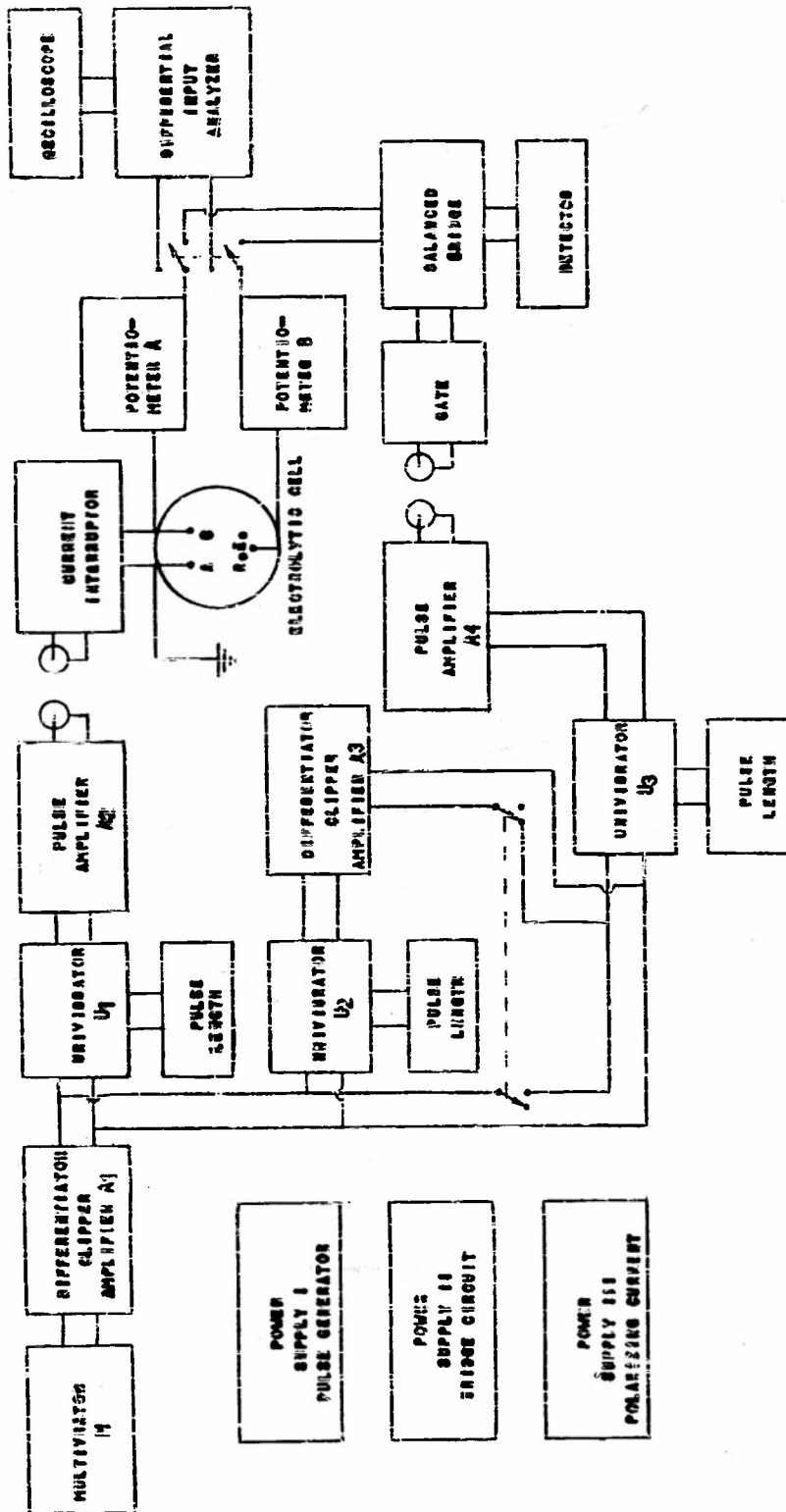
1. Polarizing current: variable from 10^{-5} through 0.50 amp.
2. Interruption frequency: variable from 2 through 20,000 per sec.
3. Interruption period: variable from 3 microsec. through 0.10 sec. or half the repetition period (whichever is shorter).
4. Duration of potential measurement: approximately one microsec. (variable if desired)
5. Accuracy of potential measurement: 1 mv. (better accuracy if measurement period is longer when using gated bridge detector).
6. Relative time of potential measurement: variable from one microsec. following current interruption through 0.10 sec. or three-fourths of the repetition period (whichever is shorter).

In addition, this apparatus provides information concerning anodic as well as cathodic polarization simultaneously.

In Figure 9 is a block diagram which indicates the function of the various components of the apparatus. Details of the circuitry for this instrument are given elsewhere.⁶ The blocks labelled M, A₁, U₁, and A₂ furnish the variable frequency square wave which controls the current interruptor I. The units in blocks U₂, U₃, A₃, A₄, and the block labelled "gate" control the time after interruption and the duration of measurement of the bridge detector. A switch permitted the direct coupled amplifier (Tektronix model 112) and oscilloscope (Tektronix model 511 AD) to visually indicate the null point. This method of detecting the null point provided a sensitivity of 5 mv./cm.

The time of interruption for most of the work was 200 microsec. which was one third the period of current flow. By means of the visual method, measurements were made within one microsec. after the cessation of the current with a time of measurement effectively zero.

Current densities were obtained by dividing the polarizing current meter readings by apparent areas accurate to within 2%. The areas were defined by glass tubing of diameter 1.013 cm. ⁺ 1%. The meter



Electronic Commutator: Block Diagram

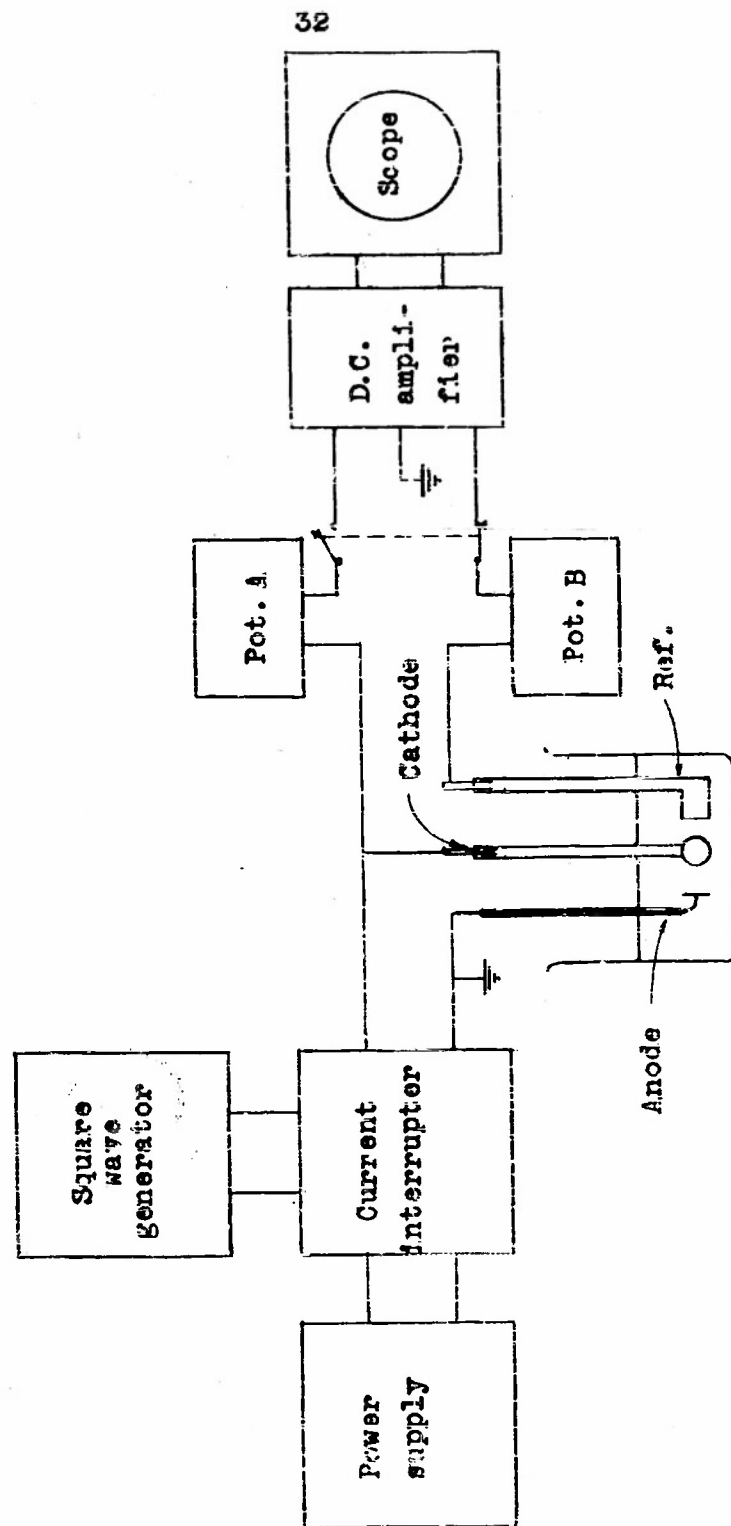
Figure 9

readings were approximately 2% accurate on the lower parts of the scale so that the relative error in the current densities was 3%.

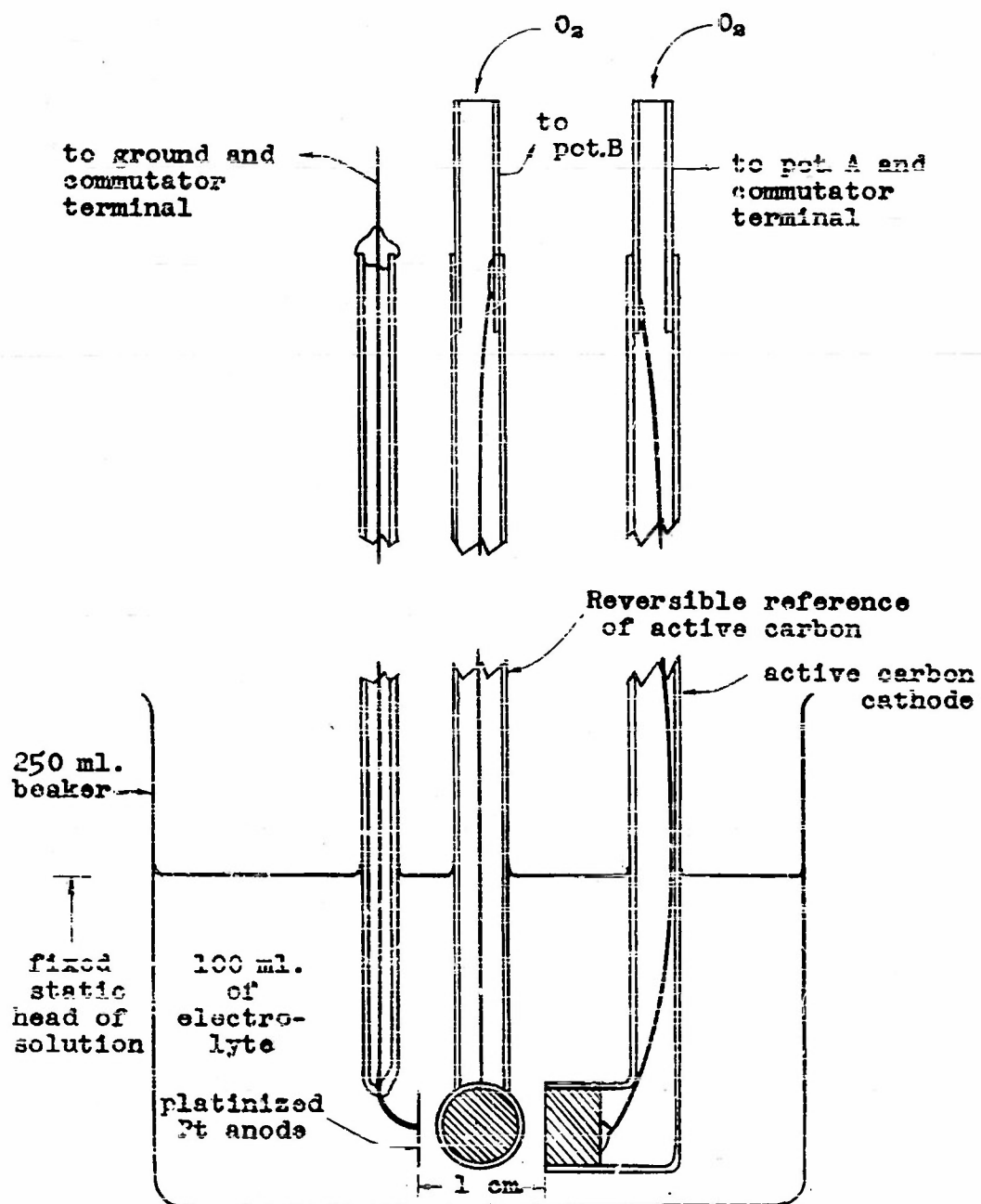
2. The Experimental Cell

A diagrammatic sketch of the cell and a condensed block diagram of the electronic apparatus showing the cell relationships are shown in Figure 10. An enlarged cell schematic is shown in Figure 11. The cell was simply an open 250 ml. pyrex beaker with the electrodes clamped in place. The separation between the anode and cathode, was limited to 1 cm. since greater distances resulted in IR drops which severely overloaded the direct-coupled differential amplifier. Smaller electrode distances were unsuitable due to interference caused by the oxygen bubbles in the vicinity of the anode. The reference electrode was located as close to the cathode as conveniently possible so that over-loading effects in the amplifier were minimized.

Oxygen was supplied from conventional high pressure cylinders through a standard reduction valve system via rubber tubing to the electrode assembly. The pressure of the oxygen fed into the back side of the electrode was measured by an open end mercury manometer, while the pressure at the electrode surface was determined by the fixed static head of the solution above it. The velocity of the gas flow was determined, therefore, by the pressure differential between the delivery pressure



Block Diagram of the Commutator, Cell, and Detector
Figure 10



Detail of Electrode Placement in the Cell

Figure 11

and the static head of the solution above the electrode.

The rate of flow of the oxygen through the plug was found to have no effect on the measurements as long as there was a slow stream of bubbles issuing through the face of the electrode. Excess gas pressure was avoided since it caused partial blocking of the face of the electrode with bubbles and in certain cases destroyed the active carbon surface layer.

One hundred milliliters of the electrolyte were placed in the cell which was supported in a thermostatic bath at $25 \pm 0.1^\circ \text{C}$. A fixed amount of hydrogen peroxide was added to the electrolyte to stabilize the static potential of the electrodes (0.01 M in H_2O_2) except where the effects of greater or lesser peroxide concentrations were desired.

Before an electrode was lowered into the solution, the oxygen gas pressure was turned on to avoid sucking electrolyte into the electrode holder. After immersion the static potential of the electrode relative to the reference was checked before being polarized.

In applications involving the use of a reversible reference, electrodes were replaced if the potential of the static cathode versus reference was 2 mv. or more.

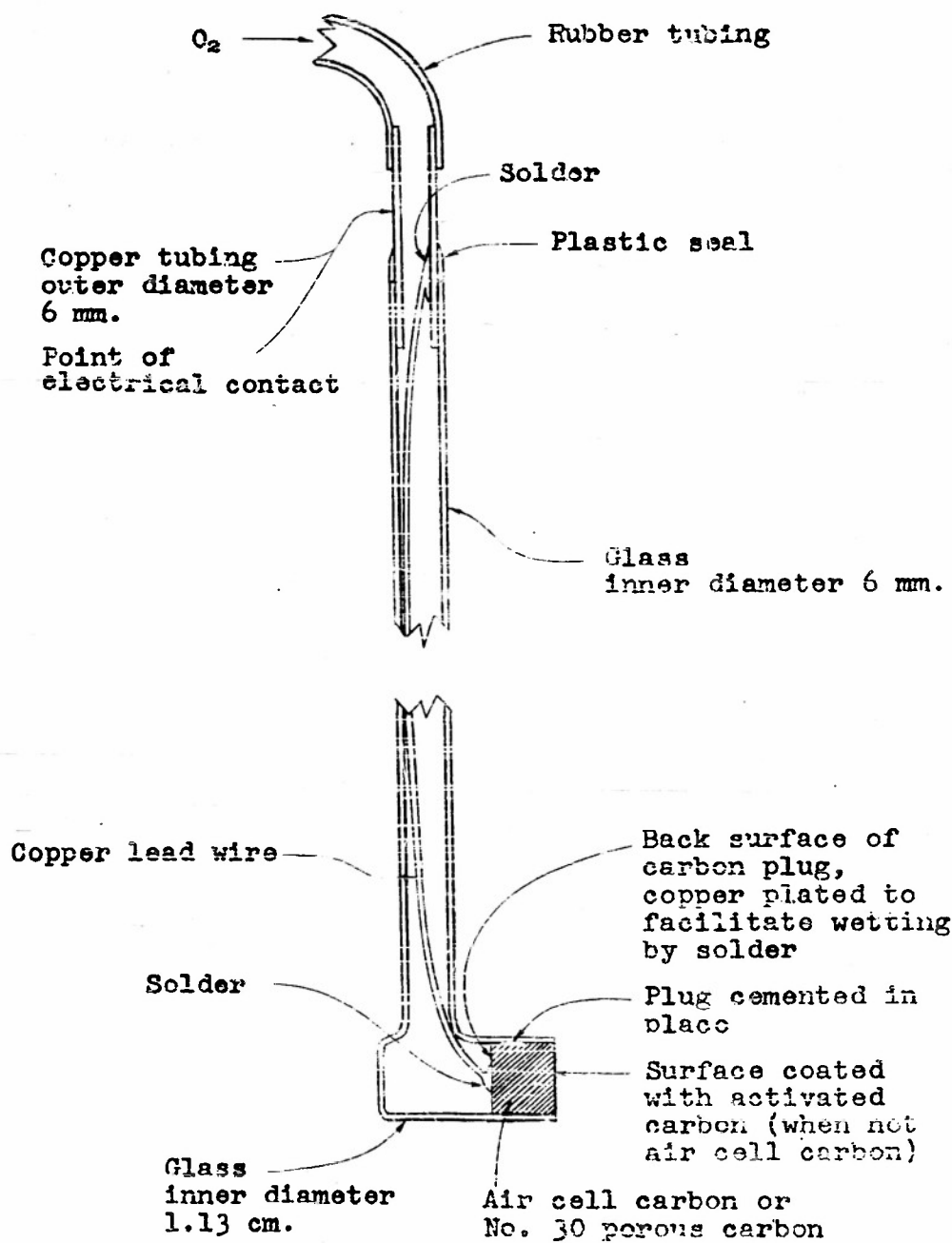
If another reference such as the mercuric oxide or saturated calomel was used, the static potential was required to agree with the theoretical value as modified by the concentrations of alkali and peroxide present.

Whether the electrode was of air cell carbon or the sprayed type (see Part II, 3a), the initial polarization was always high and drifted to a lower stable value. After the steady state of the electrode was established, the current was reduced to zero and the polarization measurements were carried out with increasing currents. On completion of the polarization measurements, the potential of the cathode versus reference was checked for agreement with the initial value a short time after the current was turned off. By subjecting the cathode to prepolarization, the polarization data were reproducible (in the case of sprayed active carbon electrodes) at all current densities.

3. Preparation of Electrodes

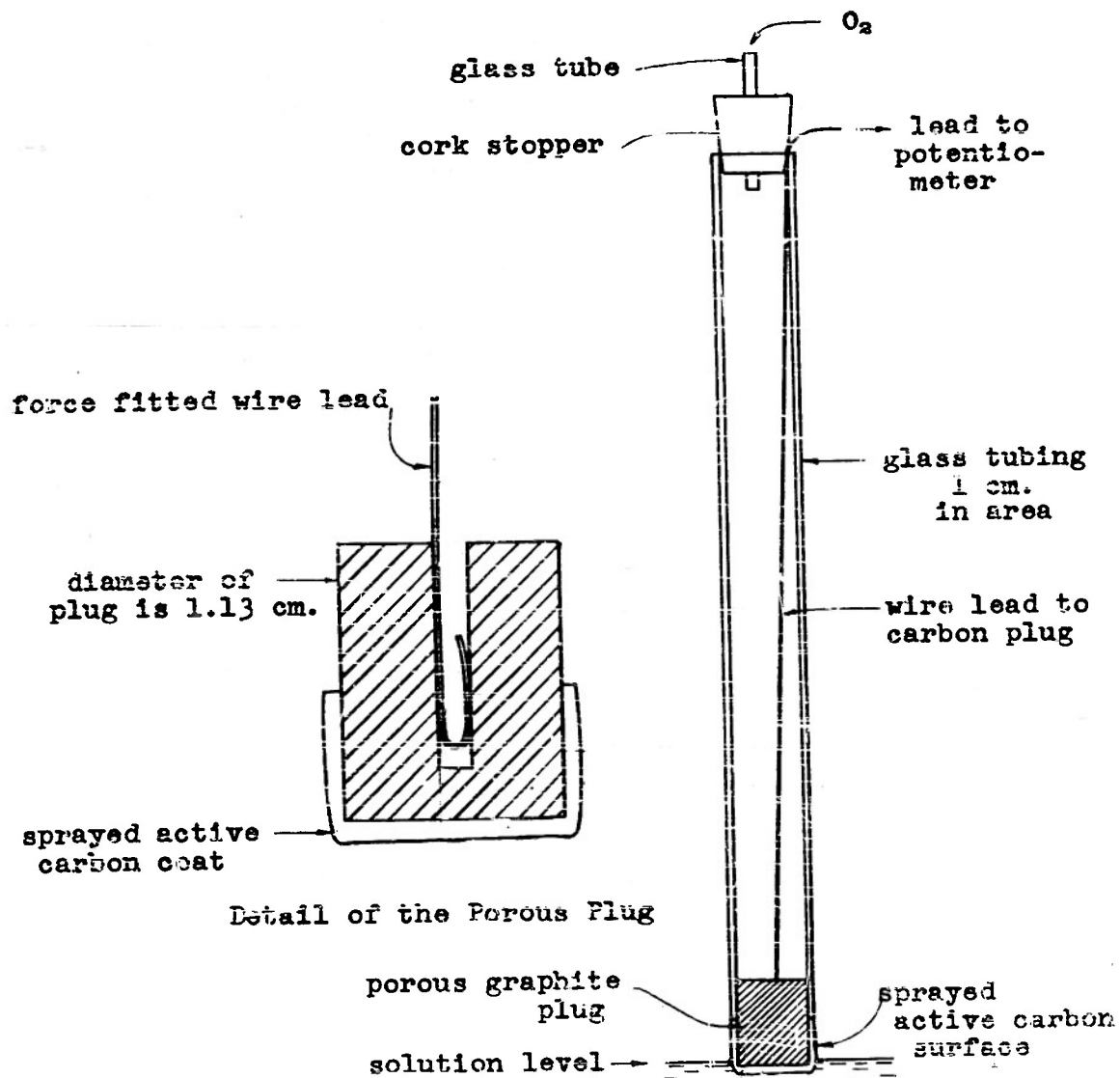
a. Electrode construction. --The electrodes used for the majority of the measurements were constructed as shown in Figure 12. The vertical section of the holder, 25 cm. in length, was of glass tubing with a 6mm. inside diameter, and the horizontal electrode arm was of 1.13 cm. inside diameter tubing giving an open end of 1 cm.². A small copper tube sealed into the upper end of the vertical tube served both as an inlet for the oxygen and as an electrical contact to the lead from the commutator.

A vertical electrode of the type shown in Figure 13 was used in static measurements.



Detail of the Electrode

Figure 12



An Electrode for Static Measurements

Figure 13

A typical electrode of commercial air cell carbon was prepared by cutting a cylindrical plug from a large air cell carbon block with a tubular cutter so that the plug was slightly larger than the glass holder mentioned above. This plug was ground to a close fit in the holder and then sealed in place either with rubber or Cenco plicene (alkali resistant) cement.

Electrical contact was made to the carbon plug by means of a spring on one end of the lead wire which was forced into tight contact with the carbon plug. The other end was soldered to the copper inlet tube. Electrical conductivity was checked after assembly by immersing the face of the electrode in a pool of mercury and measuring the resistance from the mercury to the copper inlet tube. A satisfactory assembly registered less than 1 ohm. Others were rejected.

In making electrodes with a sprayed coating of active carbon, the plug of air cell carbon was replaced with one made of porous graphite, which was cut and sealed in place in a manner similar to the above. The porous graphite used for this purpose was secured from the National Carbon Company of Cleveland, Ohio. The porosity grade most commonly used was No. 30 since the pores of this material did not plug with the active carbon particles as readily as those of the finer grades. Electrical contact in this case was made in either one of two methods. In the first a copper wire was forced into

a small hole which was drilled into the long plug of porous graphite and retained with a small drop of solder. In the second method the back end of the graphite plug was copper plated from an alkaline cyanide bath and the lead wire soldered directly to the copper layer. The copper deposit did not restrict the flow of gas through the plug to the solution. After the plug was cemented in place the lead wire was soldered to the gas inlet tube as in the case of the air cell electrodes. Of the two methods used the latter was found to be more satisfactory.

b. Application of the activated surface. --After the electrode was assembled, the active carbon was applied to the porous graphite in a manner similar to the technique of W.G. Berl¹. The active carbon material was suspended in a solution of rubber, polyethylene, or other wetproofing agents in an organic solvent such as benzene and sprayed upon the porous graphite support.

The typical carbon suspensions were made by using an active carbon of 200 mesh or finer and adding it to a hot solution of binding agent, e.g. polyethylene in an organic solvent such as benzene or toluene. The amount of binder most commonly used was 5% by weight of carbon. After mixing, the suspension was cooled to room temperature and sprayed onto the porous, supporting graphite under an infrared lamp while a slow current of air was drawn through the plug. The spraying was

continued until the coating was from 0.1 to 1.0 mm. in thickness and then baked at 120°C for ten minutes. The electrode was then ready for use.

c. Carbon materials used. --The air cell carbon used in making the preliminary measurements in NaOH solutions was obtained from the National Carbon Company in Cleveland, Ohio. This material was the positive electrode from one of their large air cells produced primarily for railway signalling purposes. The outer one-eighth inch of the block of carbon was apparently most activated. Since this material had been completely processed, it possessed considerable resistance to wetting by alkali and required no additional waterproofing

The carbon employed for making most of the oxygen electrodes was of the type used for decolorizing purposes. Purchased under the name Nuchar C from the West Virginia Pulp and Paper Company, this material had high specific volume and was finer than 200 mesh which fact made it ideal for suspensions. The actual surface area of the material was not determined, but from general factory specifications for active carbons⁷ it was probably about 800 meters per gram. Other carbons sold under the trade names of Nuchar W, Nuchar XMY, Nuchar Vegetable Charcoal, and Mallinkrodt N.P. IX Activated Charcoal were employed in suspensions as well as carbons such as animal black

⁷

E. Berl, Trans. Faraday Soc., 34, 1040 (1938).

and blood charcoal. Graphite powder from high purity spectrographic electrodes was also used for the purpose of studying a low degree of activation. The properties of these carbons will be compared in Part IV.

The application of catalyzed carbon rather than ordinary carbon in the film of the oxygen cathode resulted in decreased polarization. Carbons were prepared with silver, copper, cobalt oxide, and platinum among other metals. In a typical treatment 10 grams of an active carbon such as Nuchar C were made into a suspension with 100 ml. water. The silver was added in the form of the amino complex, the quantity depending on how much silver was desired in the final product. The mixture was then heated to 50°C. and the silver solution reduced to silver metal by the addition of sodium hydrosulphite with rapid stirring. After the suspension was filtered and washed to remove soluble salts, the residue was dried and heated until the carbon began to oxidize. The oxidation was permitted to continue while the carbon mass was stirred until about 10% loss in weight of the original carbon was incurred. The carbon was then cooled to room temperature and the binder added in the normal fashion. The suspension was then ready for use.

The above procedure was modified to deposit copper on carbon by replacing the silver salt with a copper salt before the reduction with sodium hydrosulphite.

In a similar manner active carbon has been treated

with cobalt salts so as to produce a carbon material containing cobalt oxide as the catalytic material. A suspension of the active carbon in water was treated with a solution of cobalt salts, the amount depending on how much cobalt oxide was desired in the final product. After the mixture was thoroughly stirred, the cobalt was precipitated as the hydroxide by the addition of the required amount of a base such as NaOH or KOH. The product was then filtered, washed, dried, and ignited as in the case of the silver and copper.

d. Binding agents. --The wetproofing and binding agent used for most of the early measurements was polyethylene. Several other materials which have been tried as binders for the active carbon were polystyrene, rubber, and ethylcellulose. The rubber bonded active carbon films were more adherent than the others. When binders which are soluble in an organic solvent at all temperatures were used, the carbon remained on the surface of the base material while the solvent and some of the binder flowed into the support. This resulted in an unknown binder to carbon ratio and gave poor comparisons from one electrode to another. By heating the graphite base before the spraying was begun the solvent evaporated as it was sprayed and a more uniform carbon layer resulted.

The active carbon layer obtained by this spraying technique was often quite fragile, especially in the case of the polyethylene bonded carbons, which

required somewhat careful handling to avoid damage to the active surface. The hot spraying technique was advantageous in that it resulted in more adherent layers of the active carbon as well as for the reasons mentioned above.

4. Electrolytes

The alkaline solutions were made from U.S.P. grade KOH which contained 83% KOH, reagent grade NaOH which analyzed 97%, LiOH-H₂O, and 10% tetramethylammonium hydroxide from the Eastman Kodak Company. Concentrations from 0.1 to 10 molar were used. Other electrolytes such as acids or salts were made from reagent grade chemicals.

The peroxide in the form of 90% aqueous solution was obtained from the Buffalo Electrochemical Company and diluted to about 10 M before use. The concentration of the diluted material was checked by iodometric titration. The peroxide content of the electrolytes was usually 0.01M and was increased by successive additions when desired.

5. Reference Electrodes

Three types of reference electrodes were used. For the first basic measurements with air cell electrodes in NaOH solutions, the saturated calomel electrode was employed. It was found, however, that after a relatively short period of time the electrodes became contaminated with alkali and the potential tended to vary considerably from the normal value.

A more satisfactory type reference was the Hg, HgO/KOH or NaOH half cell. These electrodes were easily prepared and reproducible to within 0.05 mv. in a short time. Such reference electrodes were stable over long periods provided the capillary tips were not permitted to dry out or the solution in them to become diluted. In addition the impedance of this type was less than the saturated calomel electrode, a factor which was important when working with the electronic commutator.

A difficulty that arises is the liquid junction potential, which can become quite large at times. Correction can be effected by calculating the junction potential or by making a series of HgO cells having the same alkaline concentration as the solution undergoing test.

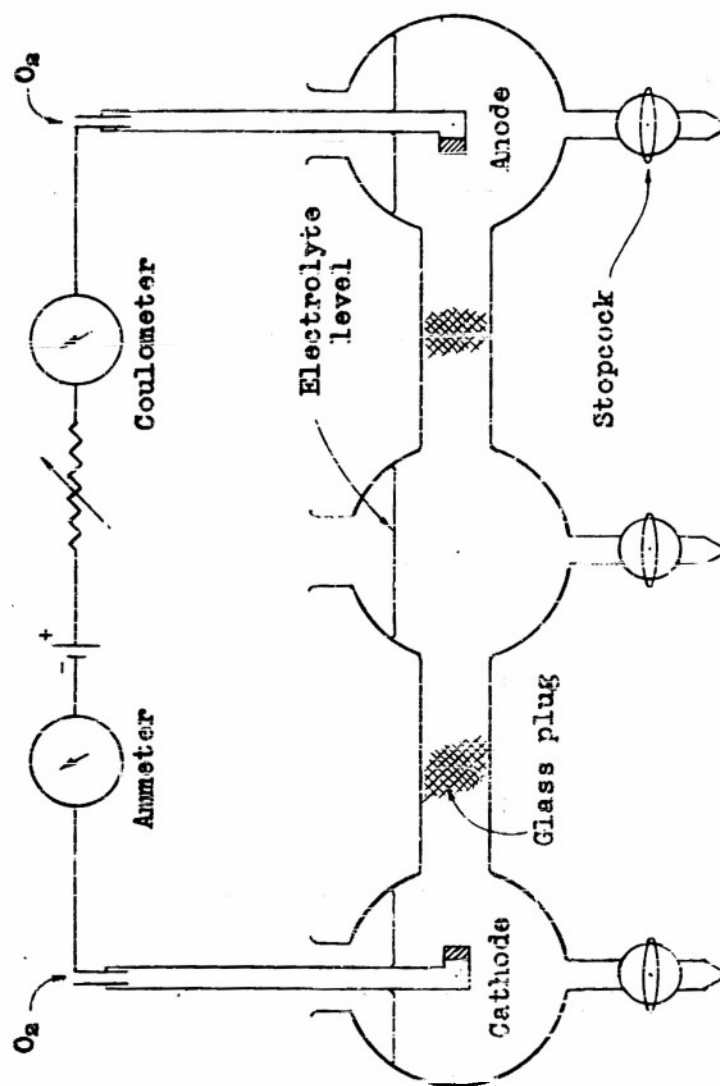
For recording absolute polarization values directly from the commutator readings without subtracting a static value, a reversible reference of the same type undergoing the polarization was used. This procedure is acceptable since it has been shown that an active carbon oxygen electrode is reversible with respect to hydroxide and perhydroxide ions.

As a safeguard during the measurements, the reversible reference was checked against an auxiliary Hg, HgO electrode and the values compared to those obtained in the static measurements.

As a second safeguard, the reference and the polarized electrode were compared for potential difference both before and after the polarizing measurement. In most cases the electrodes were found to vary less than 1 mv. after the measurements were completed.

C. The Measurement of Cathodic Efficiency

A cell and electrical circuit of the type shown in Figure 14 were used to determine the efficiency of formation of peroxide at the cathode. The cathodes were prepared from untreated active carbon bonded with 5% polyethylene. The anode was either a duplicate of the cathode or one of platinized platinum. Pure oxygen was forced through the electrode at the rate of a few bubbles per second. The anode, cathode, and middle compartments of the cell each contained 60 ml. of 1M KOH plus 0.03 M H_2O_2 . The current was controlled by the rheostat R in conjunction with the ammeter A. The total quantity of charge transferred was measured by the silver coulometer C. After 30 minutes at a current density of 50 ma./cm.² the peroxide concentration in each compartment was determined by treating an acidified portion of the electrolyte with excess iodide ion and titrating with thiosulphate. The probable error of the measurement is estimated to have been $\pm 5\%$.



Detail of the Efficiency Cell and Circuit

Figure 11.

PART III

EXPERIMENTAL RESULTS

A. Static Measurements

The static potentials of the cell (O_2 carbon | x M KOH, y M HO_2^- | satd. calomel) were measured with varying concentrations of hydroxide and perhydroxide ions. The cell was a beaker containing 100 ml. of the electrolyte, a saturated calomel reference electrode, and carbon electrodes of the standard type discussed in Part II, coated with 5% polyethylene bonded Nuchar C active carbon. All observations in this and subsequent measurements were made at a temperature of $25 \pm 0.1^\circ C$ and an oxygen pressure of approximately one atmosphere unless otherwise stated.

Agitation effects were noticed because of the differences between vertical and horizontal electrodes. With the horizontal electrodes there were no agitating oxygen bubbles issuing from the electrode face. Without sufficient stirring the values for the reduction potential were high. This can be explained in terms of the peroxide formed at the active carbon surface. In the absence of agitation, an appreciable concentration gradient with respect to perhydroxide ion was established in the solution adjacent to the electrode surface.

The Hg, HgO reference electrode gave more satisfactory results than the calomel half cell which tended to become taminated with alkali especially at high OH^- ion concentrations.

Figure 15 indicates a linear dependence of the potential on the logarithm of the perhydroxide ion concentration in 1.0, 2.5, and 5.0 M KOH. The results from these measurements check satisfactorily with those of Berl¹ and give a slope of $\partial E / \partial \log (\text{HO}_2^-)$ equal to -0.032.

The difference in static potentials between electrodes at one atmosphere and 0.21 atmosphere partial pressure was tentatively recorded as 15 mv. which is below the value of 21 mv. predicted by the Nernst equation. This can be explained in terms of oxygen released at the electrode surface through the catalytic decomposition of peroxide.

B. Dynamic Measurements

1. Behavior of Air Cell Carbon

Measurements were made on the system O_2 , air cell carbon / x N NaOH / platinized platinum with a mercuric oxide or saturated calomel reference electrode using the indirect or commutator technique described in Part II. The time required to obtain stable measurements was approximately one hour after the start of the polarizing current¹ for values of 1 to 10 ma./cm.² for the latter.

¹W.G. Berl, Trans. Electrochem. Soc., 83, 253 (1943).

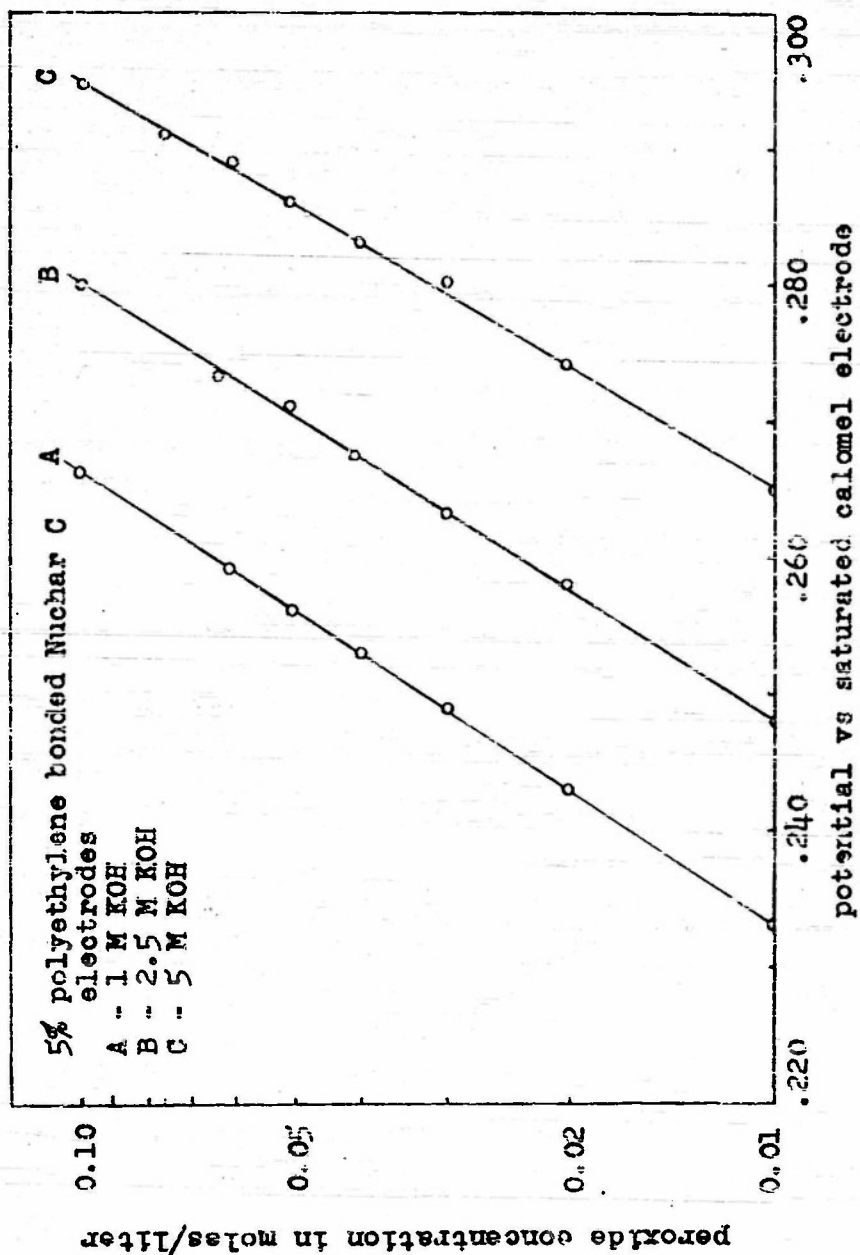


Figure 15

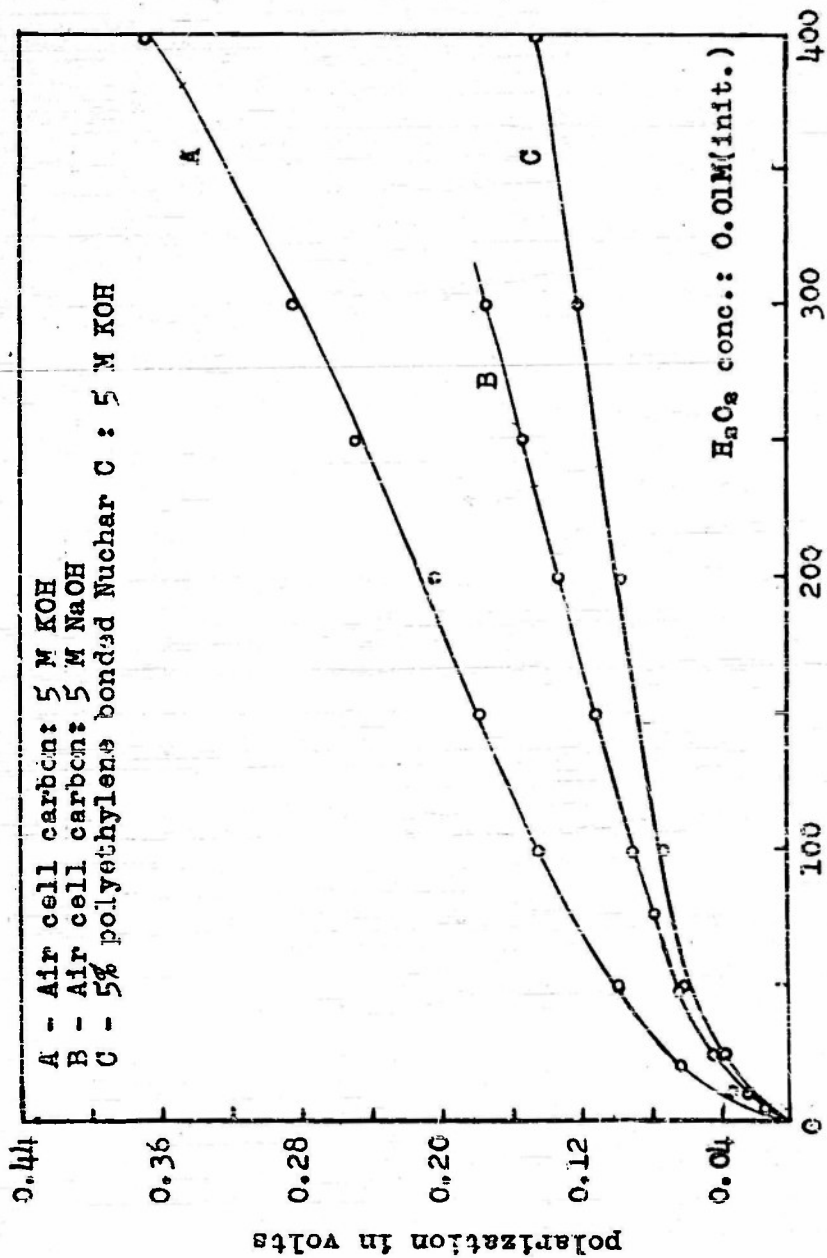
The polarizations of air cell carbon electrodes up to current densities of 400 ma./cm.² were observed in 5 M NaOH and 5 M KOH. Figure 16 indicates a decreased polarization in the NaOH. Such a characteristic has been observed only in the case of air cell carbon. In the same figure the performance of air cell carbon is compared with an improved active carbon of Nuchar C bonded with 5% polyethylene.

Figure 17 reveals the effect of increasing peroxide concentration in 1 M and 5 N NaOH at constant current density on the potential of the oxygen-air cell electrode. These data indicate that polarization decreases with increasing peroxide concentration.

2. Performance of Uncatalyzed activated Carbons

a. Binders. --The electrodes used for the majority of the measurements were of activated carbon sprayed on porous graphite and were assembled as described in the section on preparation of electrodes. The cell was the same as that discussed under air cell carbon with the exception that the reference electrodes were generally duplicates of the cathode.

Almost any adhesive material which is soluble in an organic solvent and resistant to alkali may be used as a binder. Polyethylene plastic, ethylcellulose, polystyrene, and rubber have been tested. In Figure 18 is shown a comparison of several binding agents with the



average polarizing current in ma./cm.²

Polarization of Air Cell and Sprayed Electrodes

Figure 16

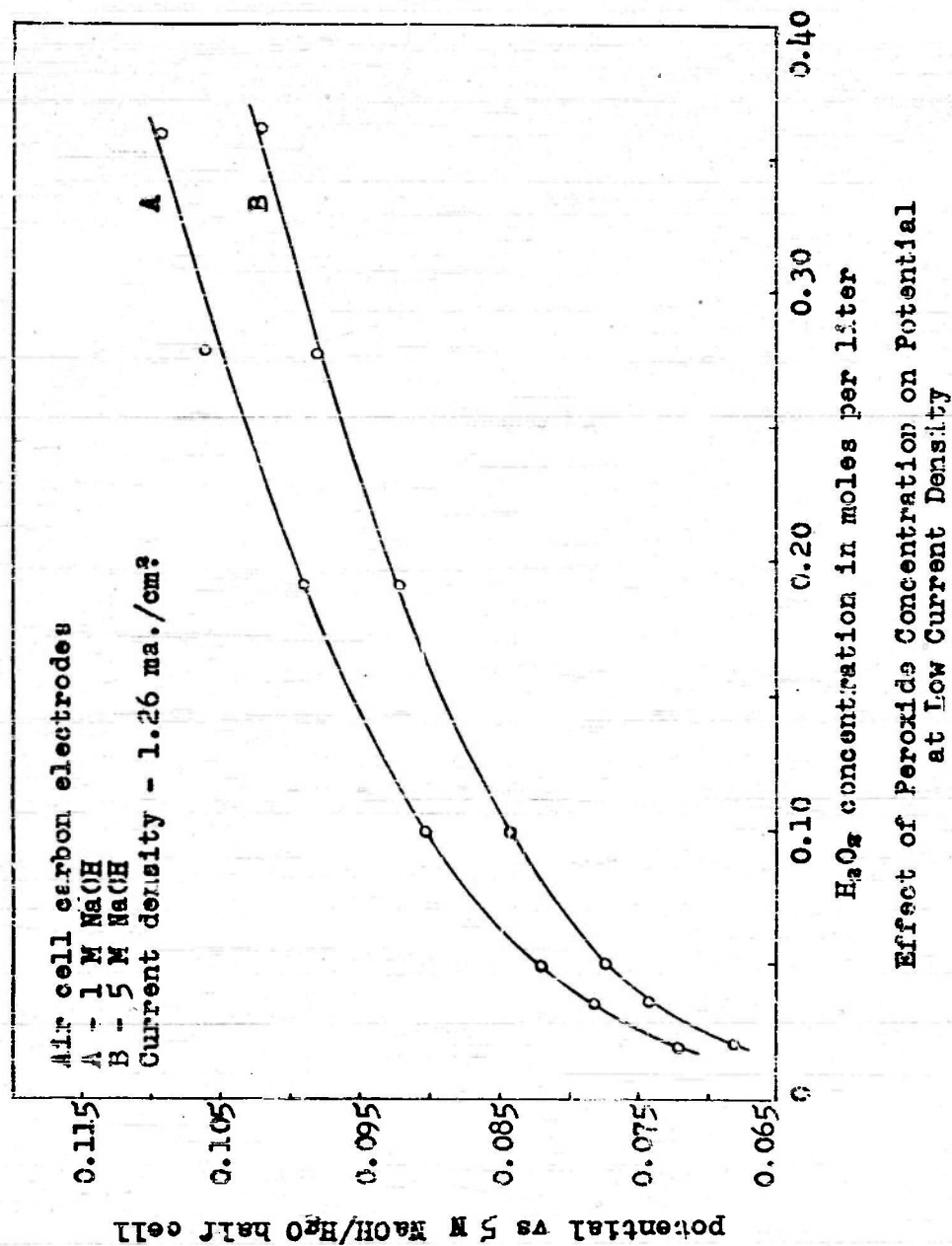


Figure 17

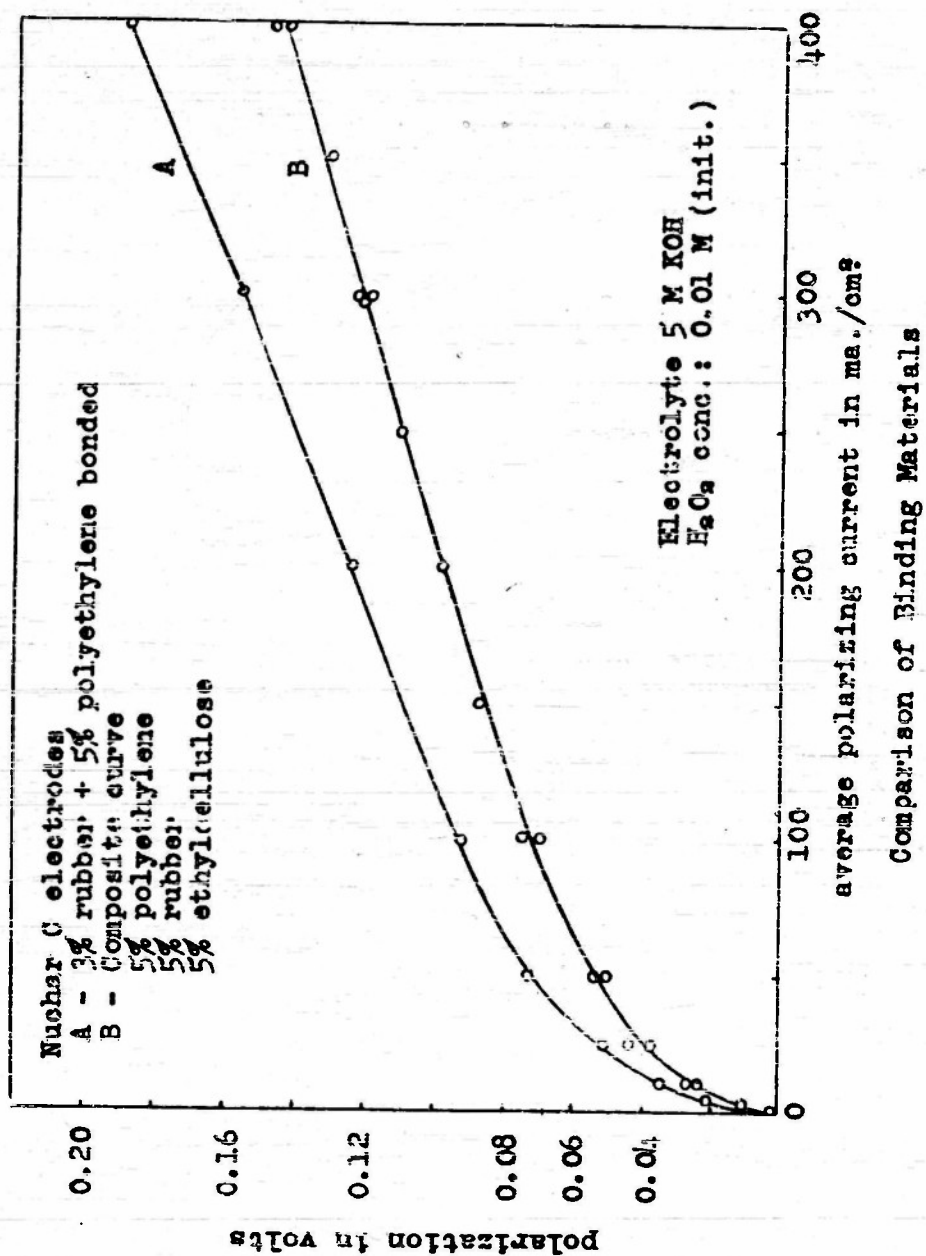


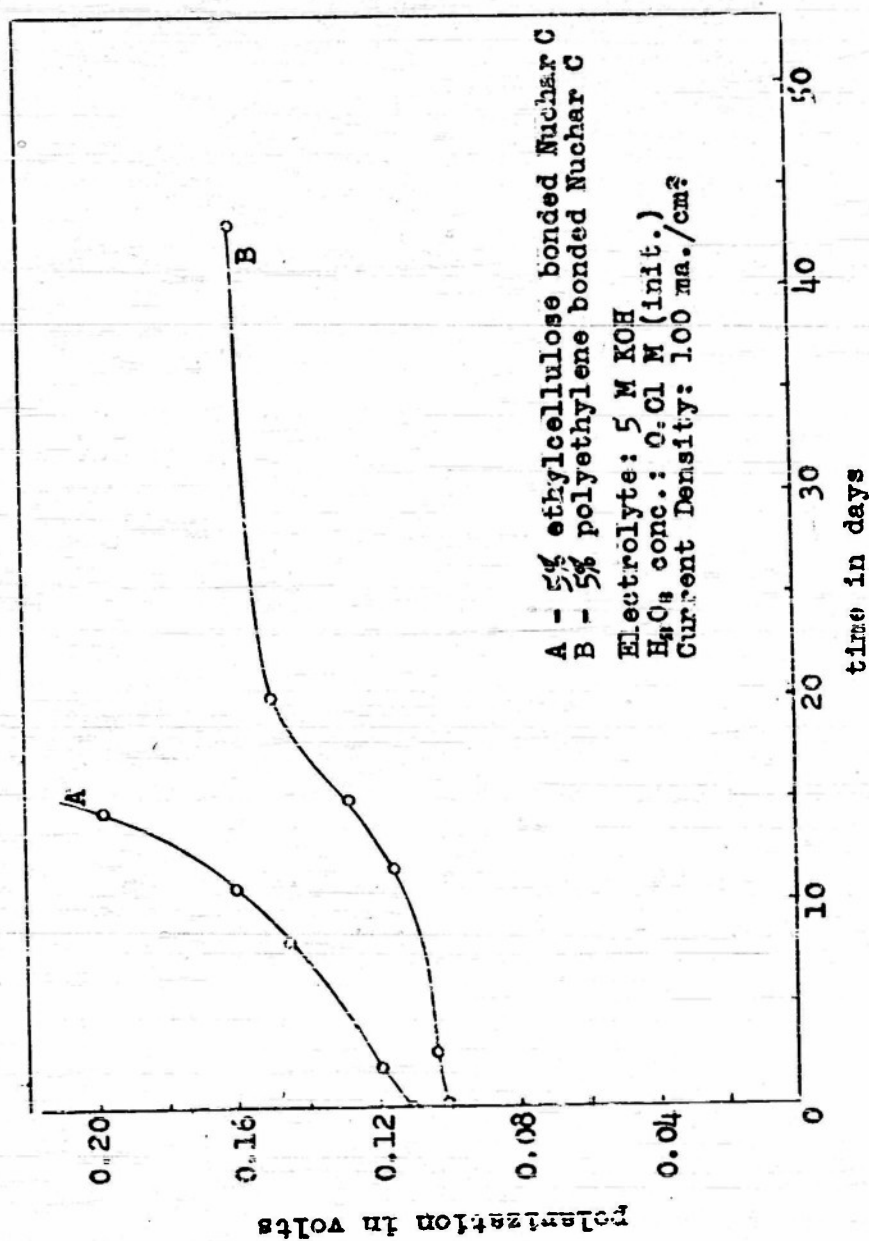
Figure 18

same active carbon material. The polarization curves for 5% polyethylene, rubber, and ethylcellulose lie on top of one another within the limits of experimental error. Quantitative data are not available for the other materials. It may be stated, however, that polystyrene though a good binder and highly resistant to alkali yields higher polarization values than the polyethylene or rubber.

The effect of increased binder concentration above is revealed in the same graph for the polarization of an electrode containing 5% polyethylene and 3% rubber. The optimum amount of binder with respect to polarization depends on the nature and specific volume of the material, and was normally 5% for activated carbons. This optimum value will be discussed later from theoretical viewpoints.

Data for the time dependence of polarization for polyethylene and ethylcellulose bonded active carbon electrodes at 100 ma./cm.² are shown in Figure 19. The polyethylene material shows a marked superiority over the ethylcellulose in that its polarization is more stable over long periods of time. Air cell carbon electrodes were not stable at 100 ma./cm.² for any great length of time.

Measurements with electrodes containing no added material other than binding agents were confined largely to electrolytes from 0.10 to 10.0 M KOH rather than NaOH solutions due to the fact that the electrodes were found to deteriorate rapidly in solutions of the latter



Time Dependence of Bonded Carbon Electrodes
at Constant Current Density

Figure 19

greater than 1 M concentration. For example, above a limit of 50 ma./cm.² in 5 M NaOH the active layer of the electrodes disintegrated. Even in cases where the active carbon was bonded with as much as 10% rubber, double the normal amount, the electrolyte penetrated the active carbon layer rapidly and the electrode became useless.

b. Comparison of activated carbons without peroxide decomposing catalysts. --

Activated carbons from the sources mentioned in Part II were found to have polarization values ranging from 60 to 150 mv. at 100 ma./cm.² in 5 M KOH and 0.01 M H₂O₂.

Polarization vs. current density curves are shown in Figure 20. The binder and wetproofer were polyethylene in each case. The superior Nuchar C was 3.4% ash which is in the process of being analyzed. The x-ray diffraction pattern of this material indicated an amorphous carbon structure with little or no graphitization present. The high activation and low polarization of this activated carbon were associated with its high specific volume among other factors.

A rough qualitative evaluation of active carbons was made by measuring the short circuit current yielded by a cell of the type.

air, active carbon/ 5 M KOH / Zn

The active carbon cathodes were constructed so as to present a 1-cm.² apparent area to the electrolyte. Results from these tests showed that spectroscopically pure graphite was very poor. Active carbons with trade names Nuchar W,

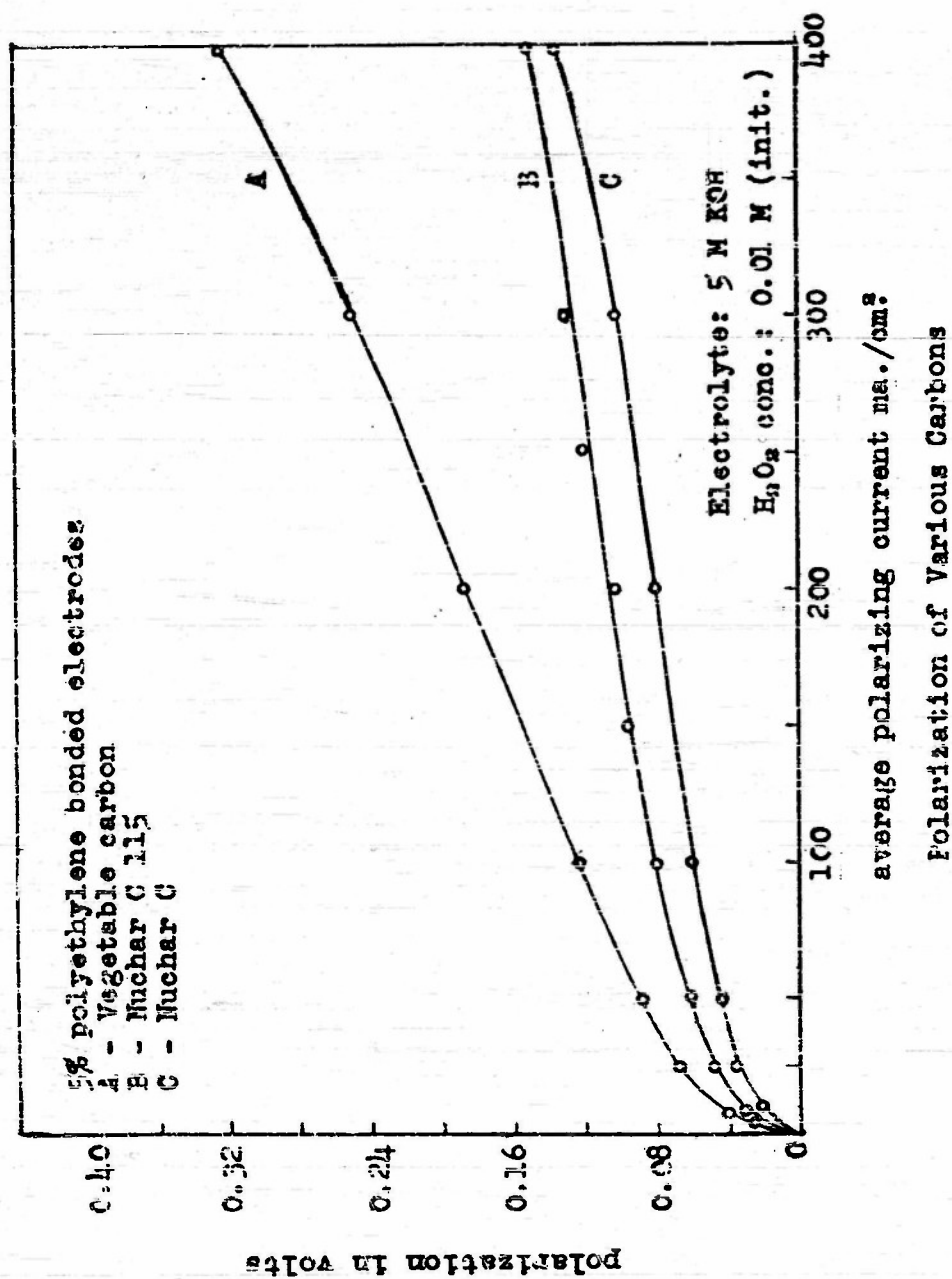


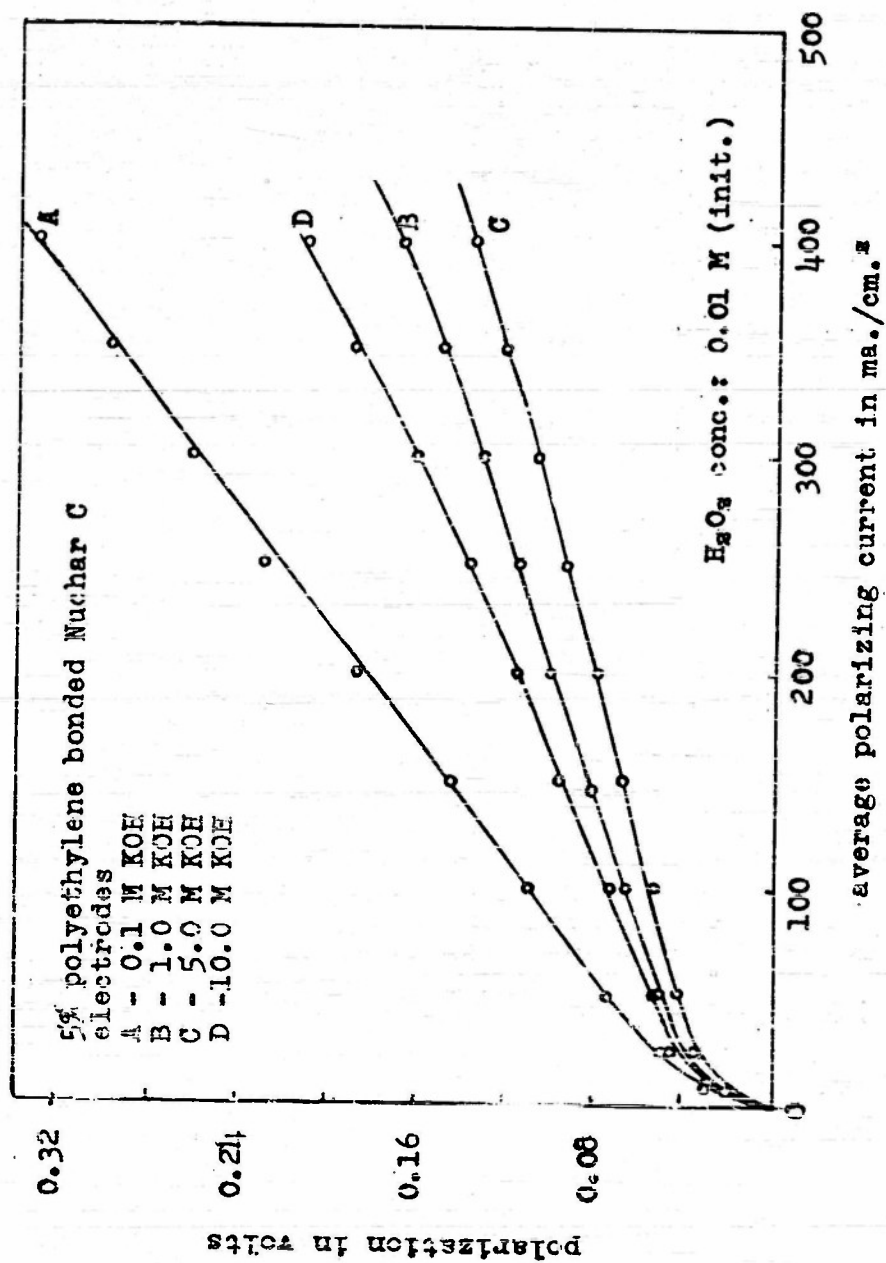
Figure 20

Nuchar vegetable charcoal, and Mallinkrodt N.F. IX activated charcoal were inferior to the products Nuchar C 115, and Nuchar C which yielded short circuit currents over 600 ma./cm.²

c. Effects of varying pH and salt concentrations---

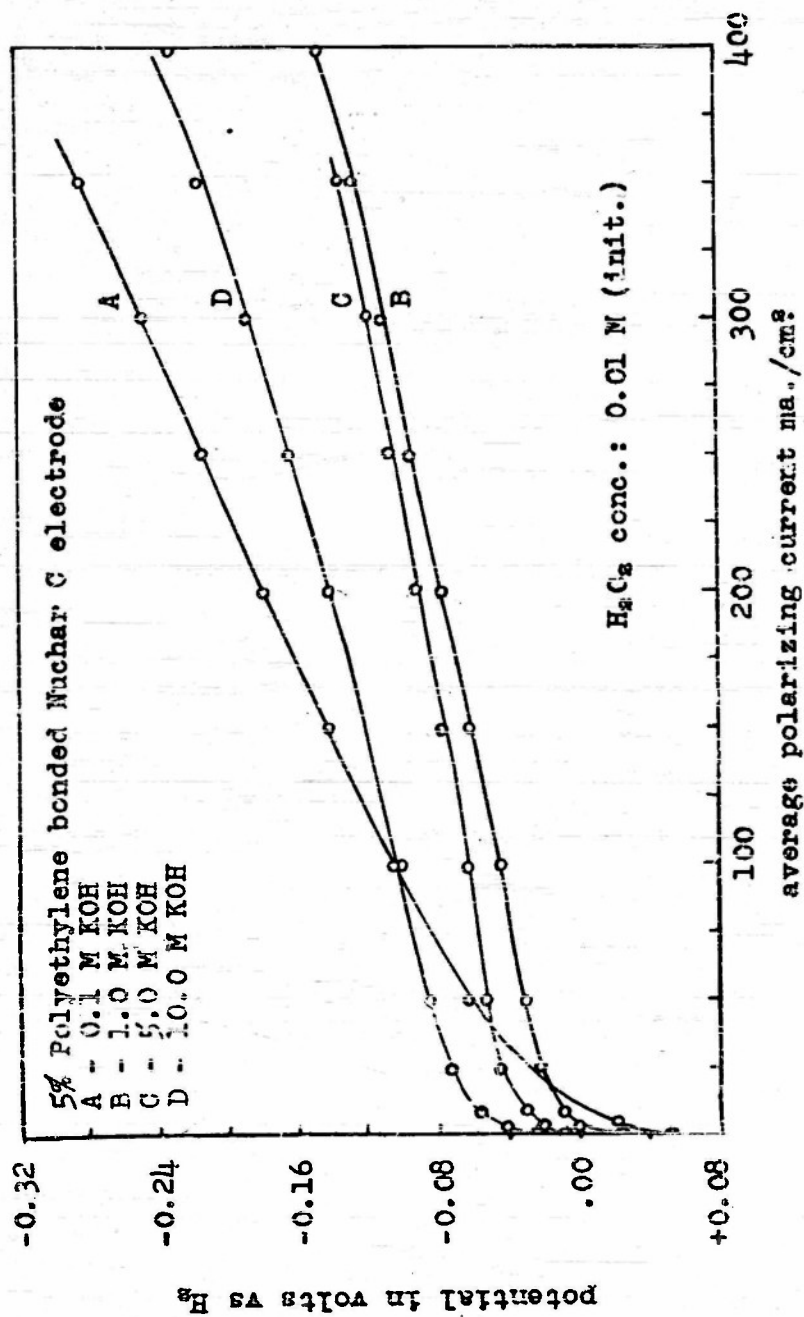
The effects of changing the concentration of KOH while maintaining the same initial concentration of peroxide are shown in Figure 21. These results show the polarization passes through a minimum at or near the maximum conductivity of the solution. The potential current curves are shown in Figure 22 for the same conditions. The static values follow the dependence of the Nernst equation on the concentrations of hydroxide and perhydroxide ions, the more concentrated alkali having the lower reduction potential.

Figure 23 illustrates graphically the behavior of a rubber bonded electrode in 1 M NaOH and 1 M KOH. The ratio of the slopes of the linear portions of the curves compared with the ratio of the resistivities differ by only 9%, a fact which at first may seem surprising but which will be explained in Part IV. On the other hand, Figure 24 which compares the polarizations of a similar electrode in 1 M LiOH and KOH indicates, at least in the more stable low current range, that the lithium and potassium curves can be imposed within the limits of experimental error. On the same graph is plotted the curve of another electrode in tetramethyl ammonium hydroxide. The conductivities of molar lithium, sodium, and potassium hydroxides



The Effect of KOH Concentration
on Polarization

Figure 21



Dependence of Potential on KOH Concentration

Figure 22

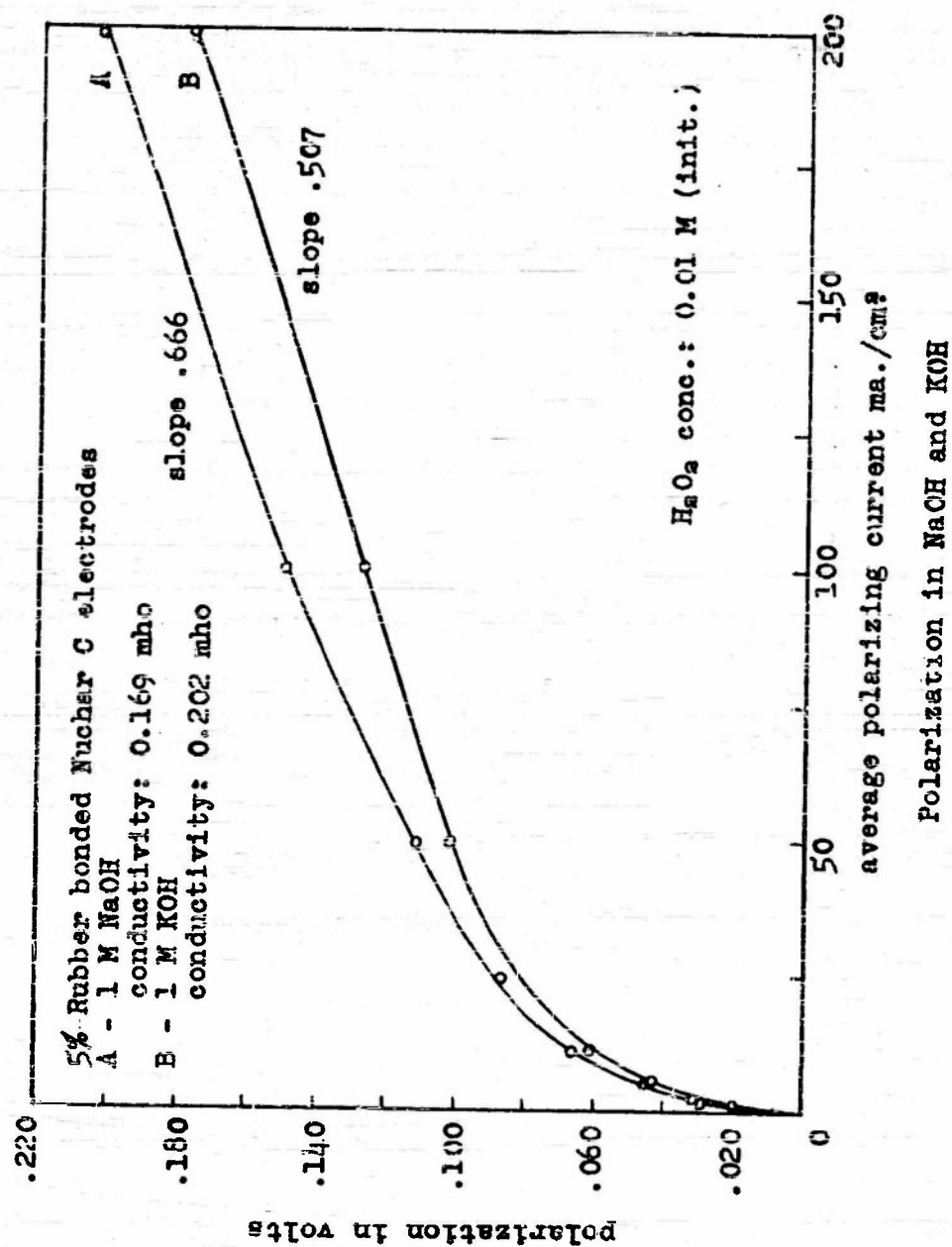


Figure 23

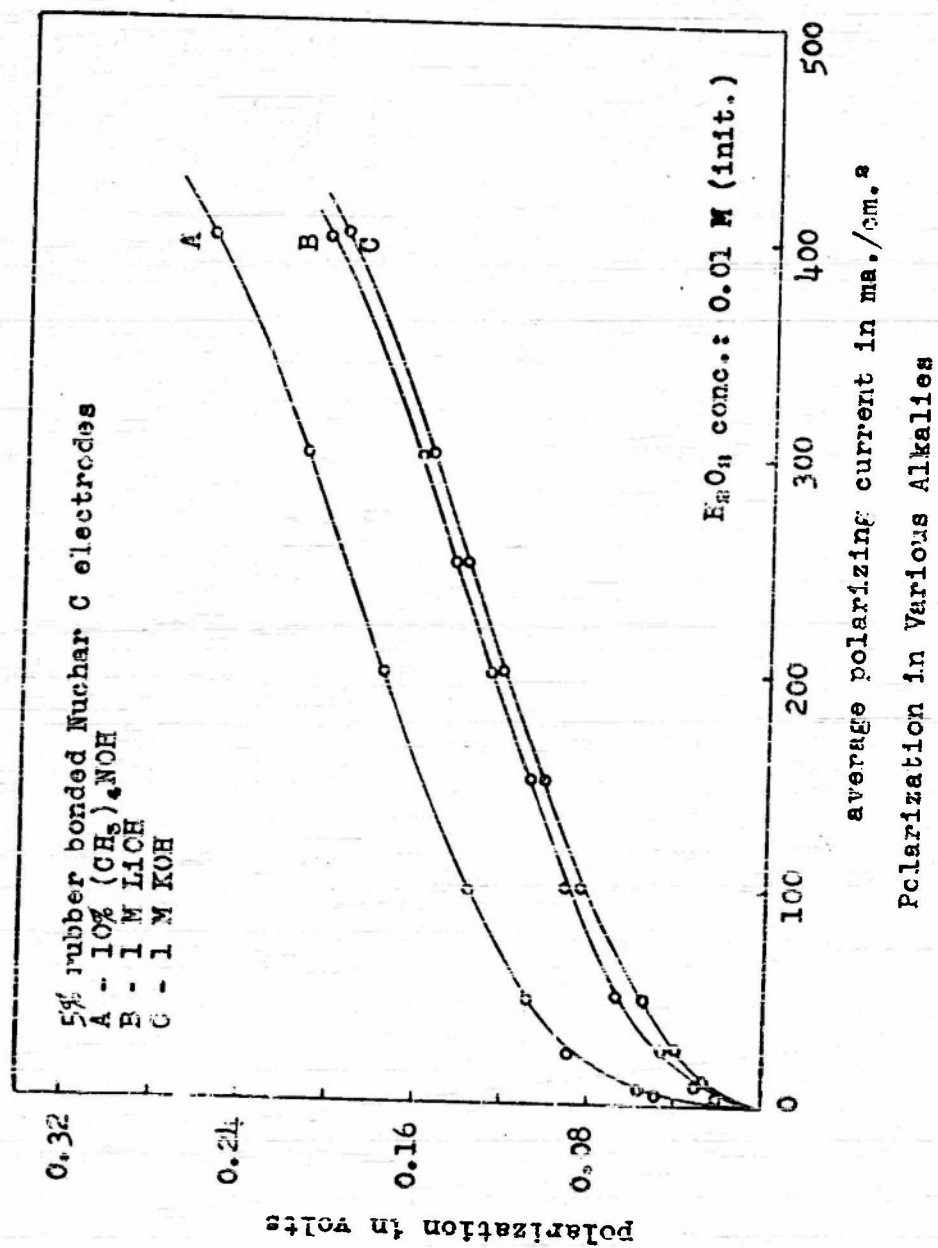


Figure 24

are 0.14, 0.17 and 0.20 respectively. In most measurements the more conducting solution had less polarization if not a flatter slope.

The resistivity ratios and the slope ratios in Figure 25 for the polarizations of rubber bonded carbon in 1 N KOH and 0.5 M KF are 1.4 and 1.7 respectively.

Potential vs. current curves in the neutral and acid pH ranges are shown in Figure 26. They are characterized by abrupt slopes at low current densities and flattening slopes at increasing current densities. The steepness of the initial slope is generally larger with decreasing pH.

d. The effect of varying peroxide. --The effect of increasing peroxide concentration on polarization is shown in Figure 27. The two curves were obtained with peroxide concentrations of 0.012 and 0.124 M in 5 M KOH. The curve corresponding to the higher peroxide concentration has the less polarization as would be anticipated since the peroxide concentration also changes the reversible potential.

The effect of peroxide on an electrode being polarized at a constant current density of 100 ma./cm.² is shown in Figure 28. In this case peroxide was added in successive amounts until the polarization reached a minimum value. A logarithmic plot of the same data of Figure 28, i.e., polarization vs. $\log H_2O_2$, gives a straight line for peroxide concentrations up to 0.25 M, is shown in Figure 29.

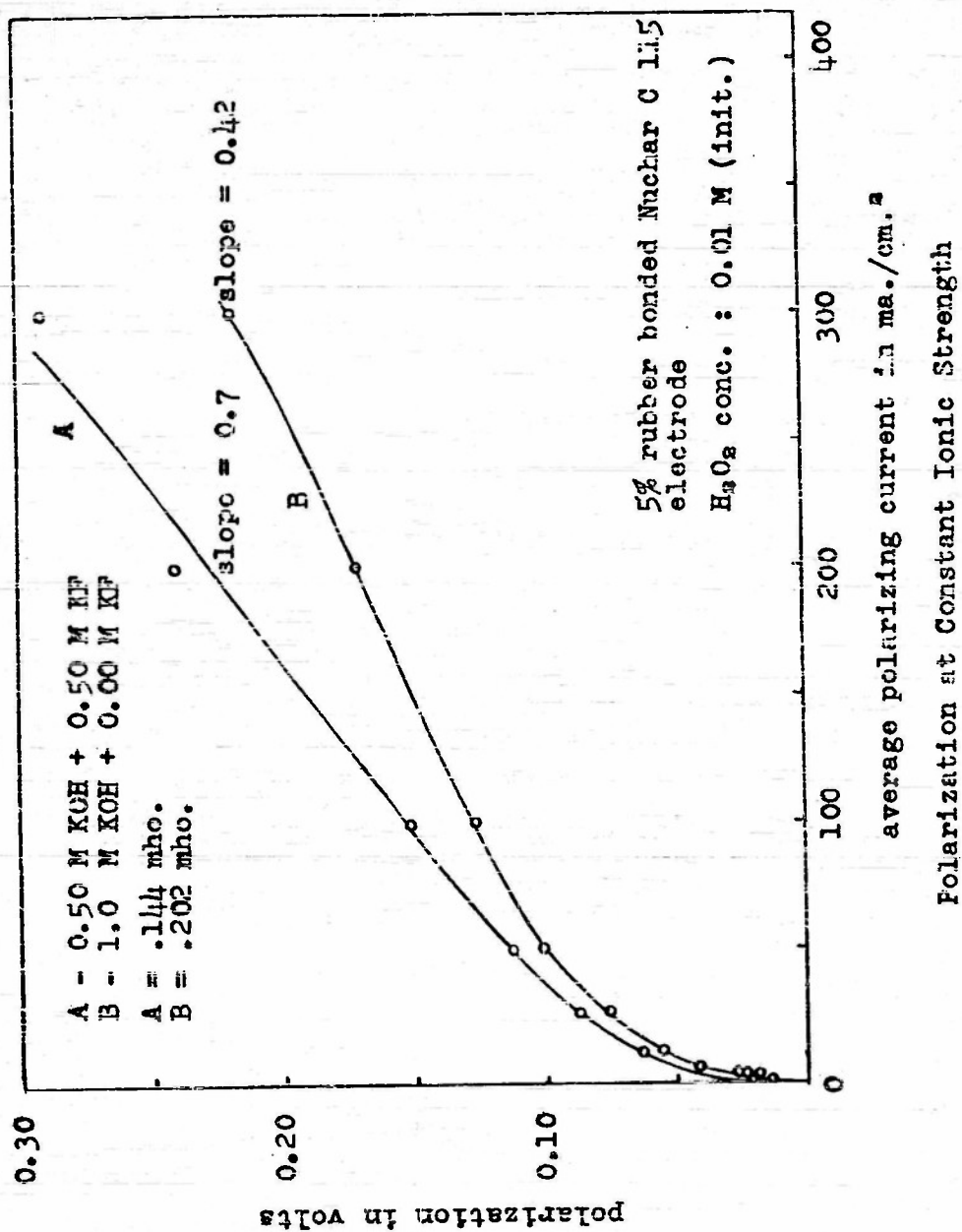
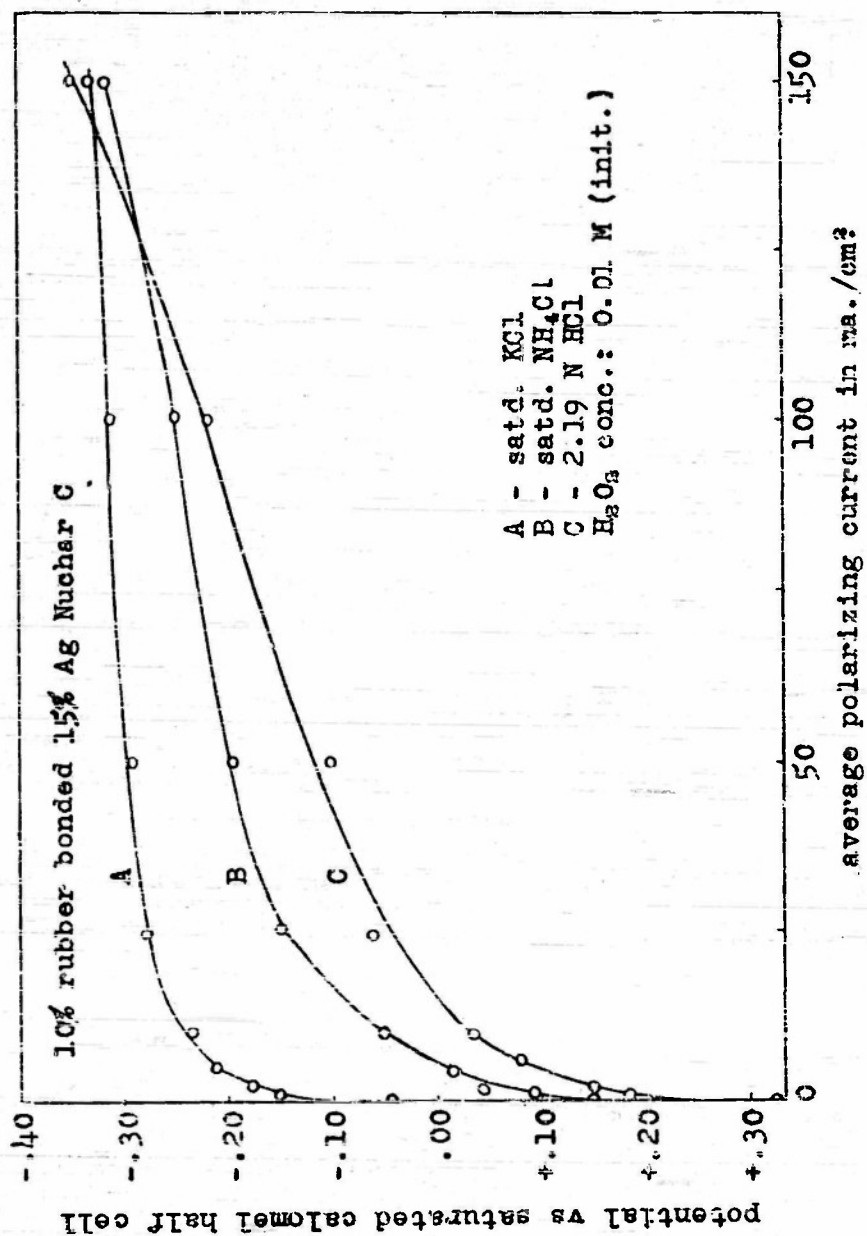
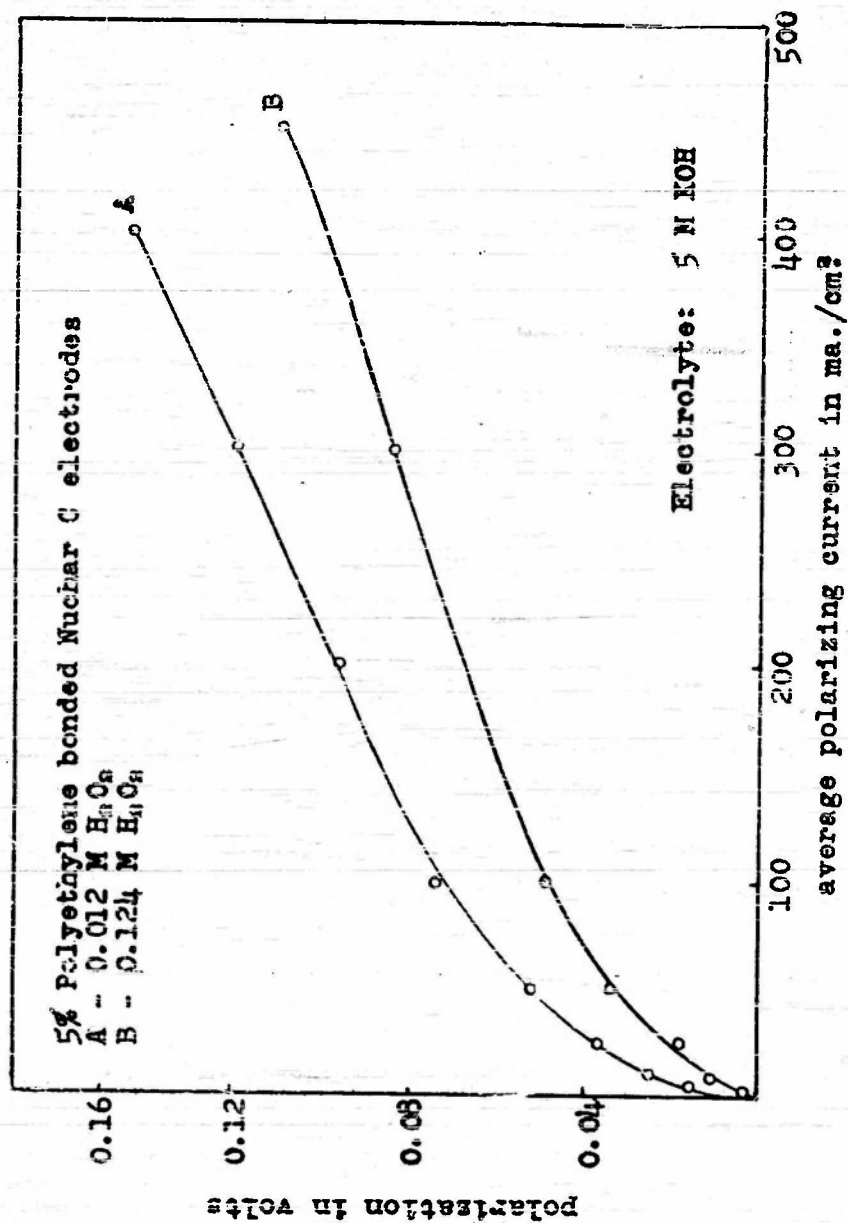


Figure 25



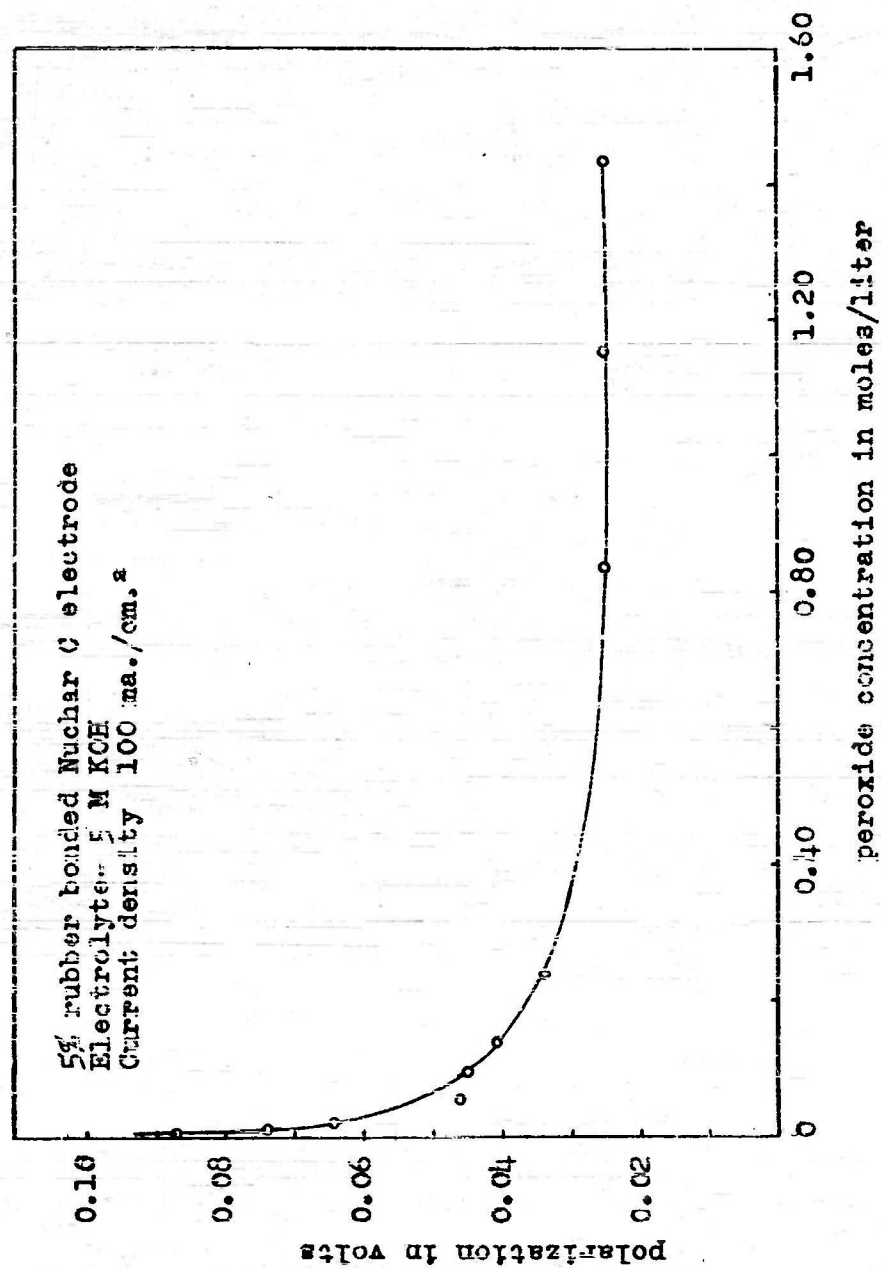
Potential-Current Relationships in Neutral and Acid Electrolytes

Figure 26



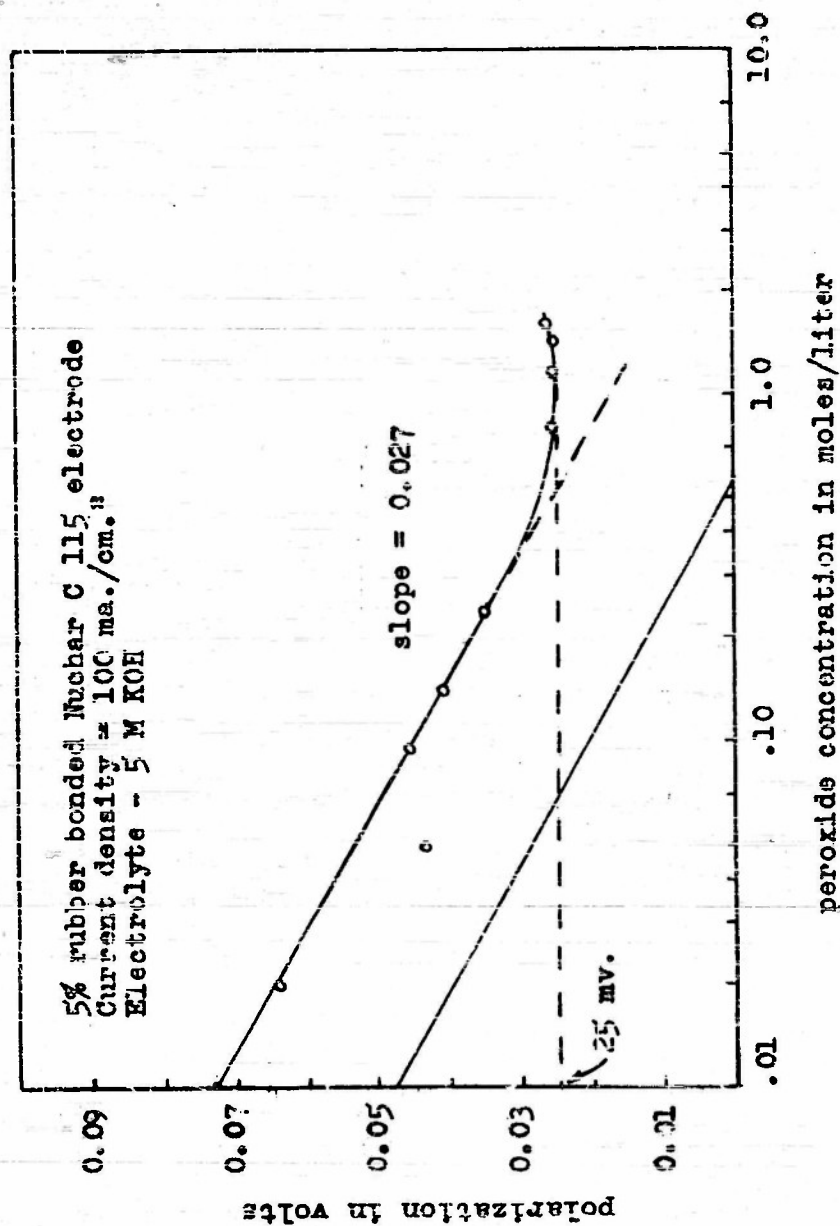
Effect of Increased Peroxide Concentration on Polarization

Figure 27



The Effect of Peroxide on Polarization
at Constant Current Density

Figure 28



The Effect of Peroxide Concentration on Polarization
at Constant Current Density

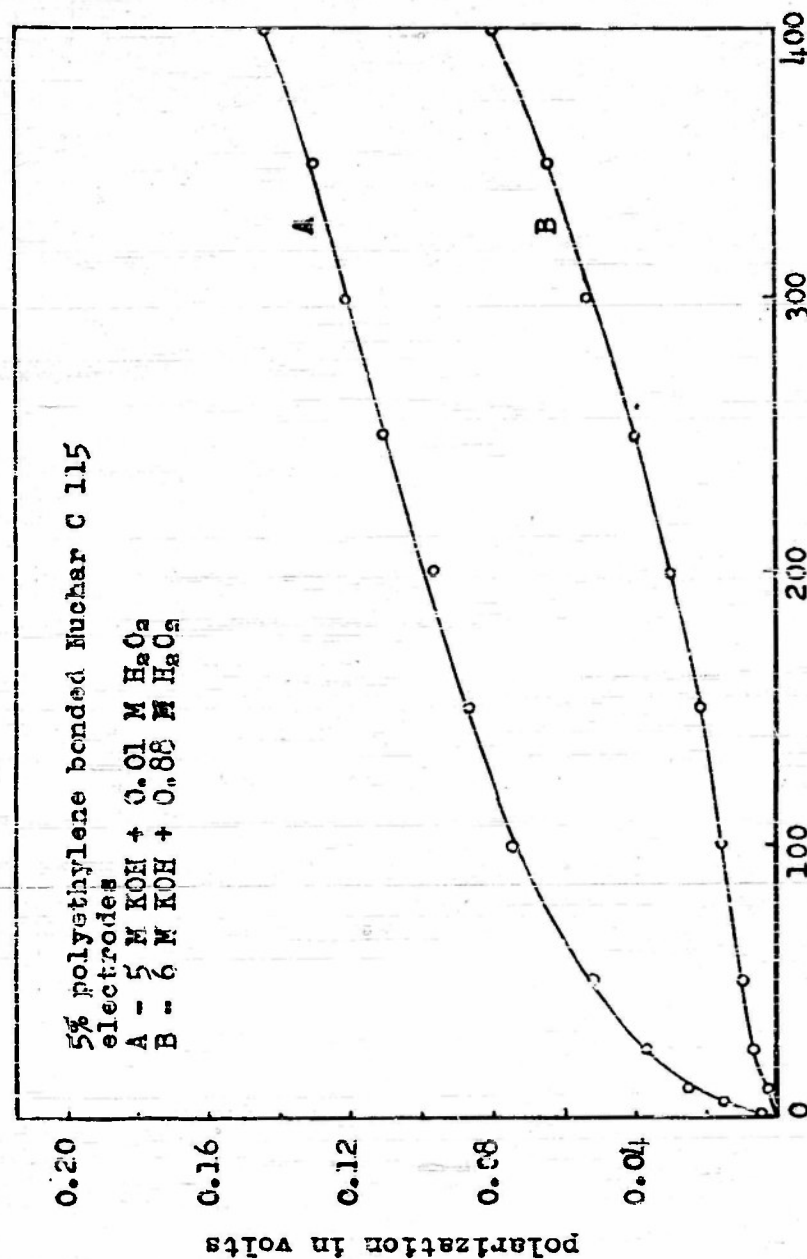
Figure 29

A curve of some interest (because a straight Tafel line has been obtained from the semilogarithmic plot) is shown in Figures 30 and 31. The unusually high concentration of 0.88 M peroxide in 6 M KOH was obtained by mixing 45% peroxide with the required base concentration while cooling the mixture.

The concentrations of both the peroxide and hydroxide were determined immediately after completing the measurements. The exchange current was found to be 4 ma./cm.² and the Tafel slope was 0.01. These results will be discussed again under interpretations.

e. Effects of oxygen pressure. --The effect of oxygen pressure on cathodic polarization was studied in 5 M KOH and 0.01 M. H_2O_2 . Pure oxygen at 1 atmosphere and air with a partial oxygen pressure of 0.20 atmosphere were introduced into the electrode. The curve at 0.20 atmospheres is characterized by a rapid rise in the polarization near 350 ma./cm.² which is indicative of a limiting current (see figure 32). The flat curve for oxygen at 1 atmosphere partial pressure is predicted to rise in a similar fashion at higher current densities.

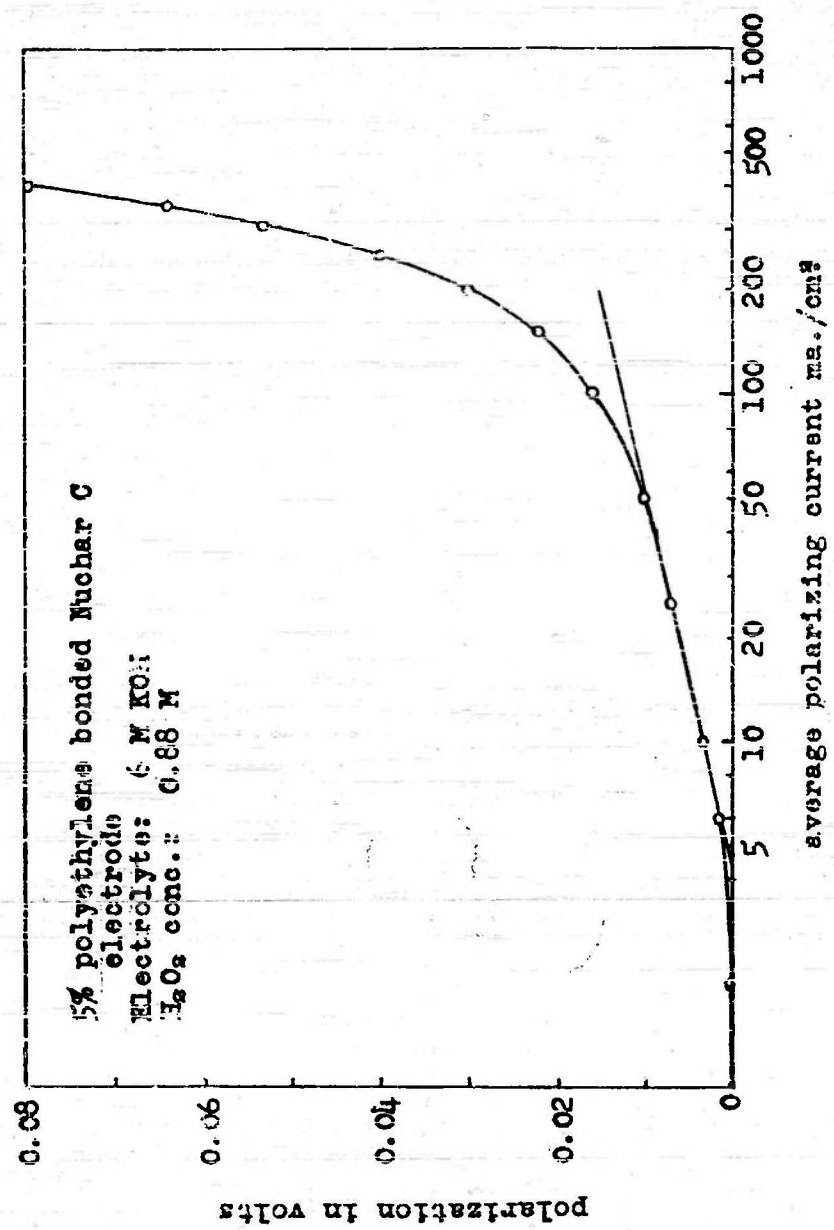
f. Temperature effects. --Only tentative temperature dependence measurements have been completed at the present time. These indicate a temperature coefficient for the polarization of approximately 0.50 mv./°C at a current density of 200 ma./cm.² in an electrolyte of 5 M KOH plus 0.12 M H_2O_2 in the range 21 to 52° C.



average polarizing current in ma./cm.²

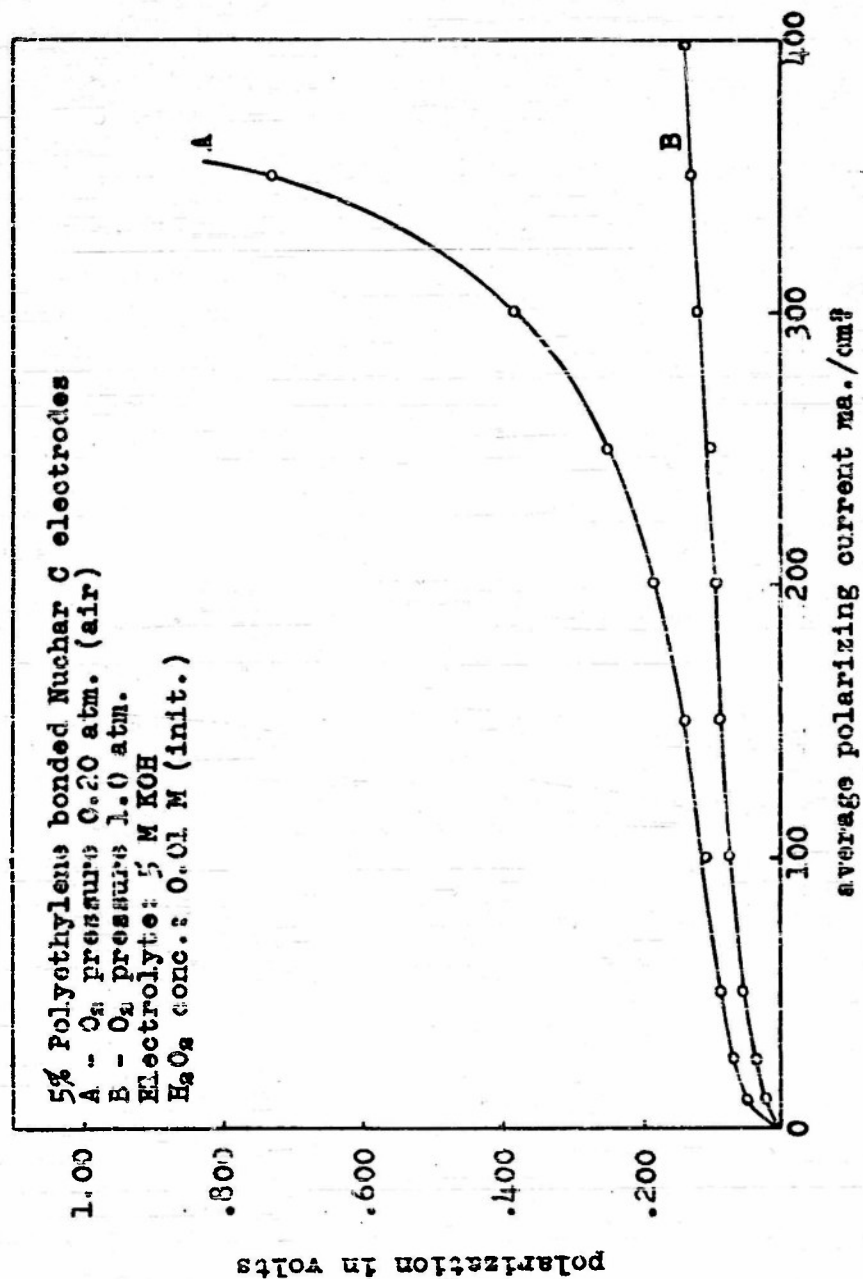
Polarization at High and Low Peroxide Concentrations

Figure 30



Polarization at High Peroxide Concentration

Figure 31



Effect of Oxygen Partial Pressure on Polarization

Figure 32

g. Current efficiency of peroxide formation. --

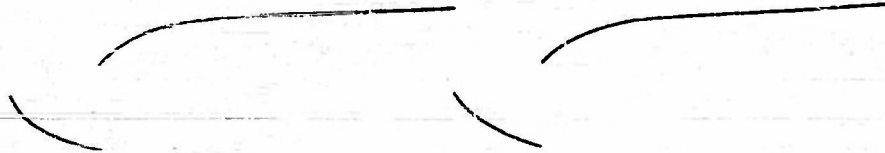
Using the efficiency cell described in Part II, a measurement with a cathode made of 5% polyethylene bonded Nuchar C was made in 1 M KOH in the peroxide concentration range 0.020 to 0.025 M. The experiment yielded 85%-87% for the current efficiency of peroxide production at 50 ma./cm.²

h. Cathode decay traces. -- Typical decay traces are shown in Figure 33 with the ordinates representing potential and the abscissae time. Figure 33 illustrates the reference vs. anode trace while Figure 33b shows the cathode vs. anode trace. The interruption periods were 200 microsec. in length. The decay curves are plotted together in Figure 33c to indicate the subtraction which was performed electrically with the differential amplifier to obtain the tabulation below. The amount of vertical fall of the left side of the trace is indicative of the degree of reversibility according to Grahame.² Decay values for the cathode reference trace, are tabulated below for a catalyzed and an uncatalyzed active carbon electrode.

Type carbon	Decay
Nuchar C	15 mv. at 100 ma./cm. ² (200 usec.)
Nuchar C 15% Ag	8 mv.

² D.C. Grahame, J. Phys. Chem., 57, 287 (1953).

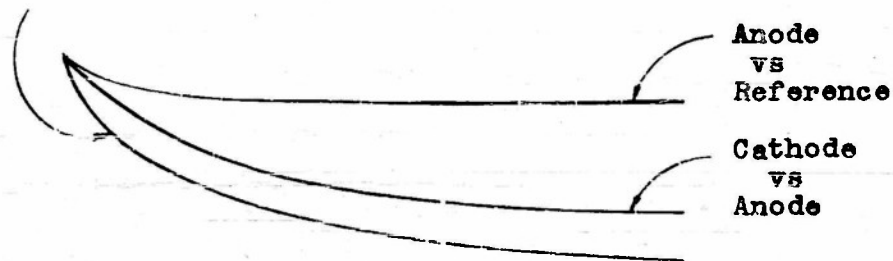
(a) Cathode vs anode



(b) Anode vs reference



(c) Cathode vs reference



Oscilloscope Decay Traces

Figure 33

3. Active Carbons Electrodes with Peroxide Decomposing Catalysts

a. Catalysts. --The poor behavior of the uncatalyzed carbons in NaOH solutions has been remedied in large part by the use of catalyzed carbons. The best results have been obtained with active carbons treated so as to give a highly "intimate" combination of the carbon with silver metal or cobalt oxides. Of the two materials, silver is superior in terms of decreased polarization and low penetration of the electrolyte into the active carbon at both high current densities and high alkali concentrations. Copper or iron proved to be of either minor or negative benefit while platinum seemed promising.

The optimum amount of silver was found to be about 15% by weight of carbon. This value was arrived at by means of the rapid test method described in Part II. A comparison of the outputs for electrodes containing 5, 10, 15, 25, and 50% silver by weight of carbon indicated the existence of a minimum polarization at about 15% silver.

In order to increase the mechanical strength of the silvered carbon films, 10% rubber was incorporated as the binding material.

b. Comparison of catalysts. --A comparison of polarization curves for the uncatalyzed active carbon with 5% binder and the 15% silver activated material indicates the superior performance of the latter (Figure 34).

Figure 35 compares the potentials vs. current

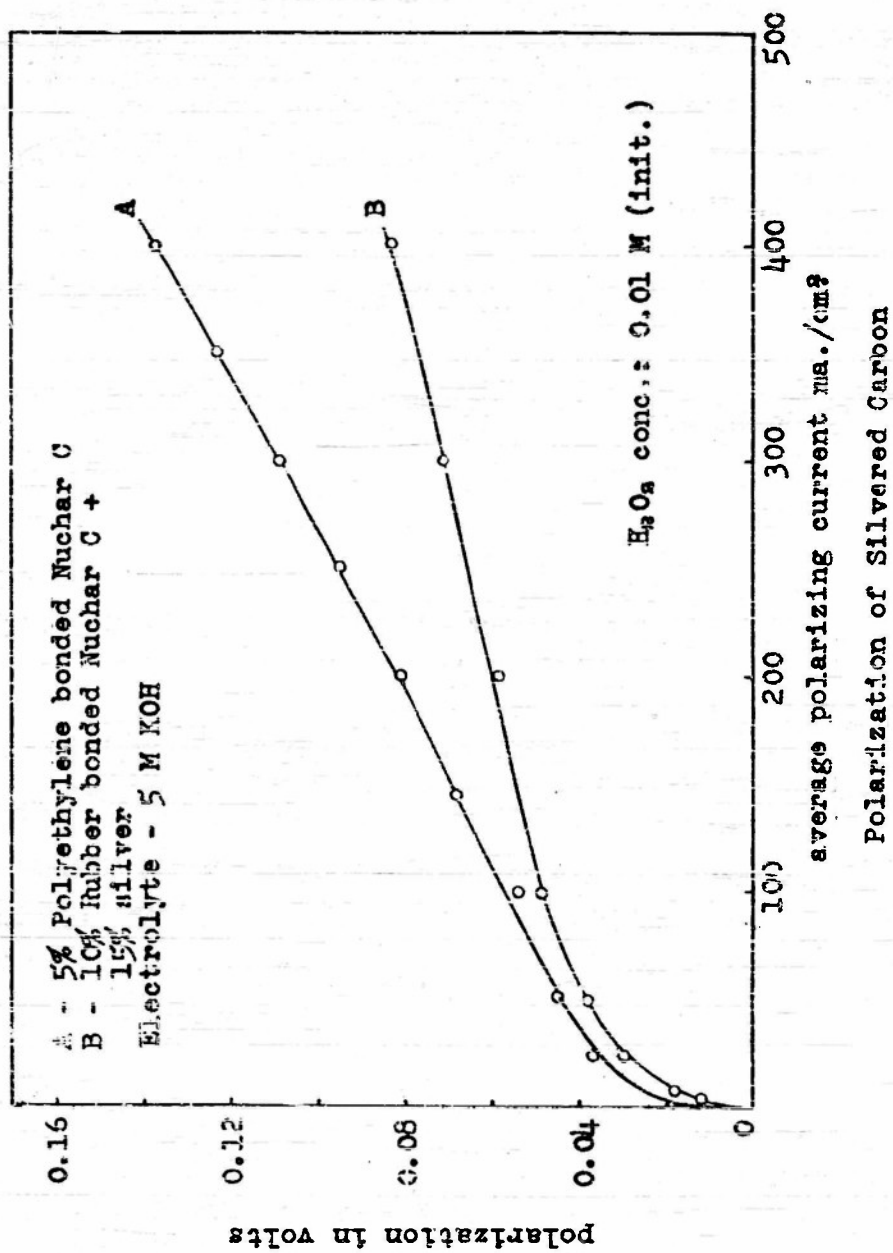


Figure 34

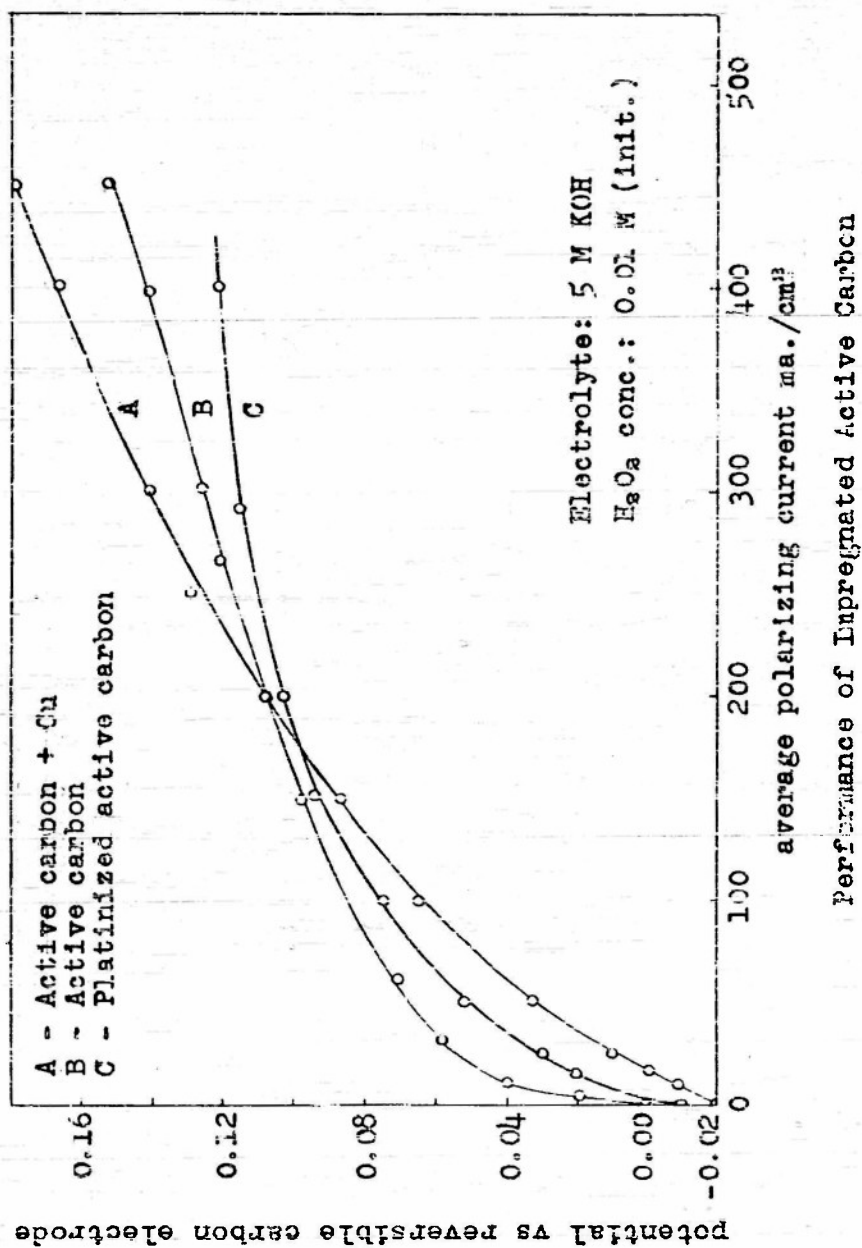


Figure 35

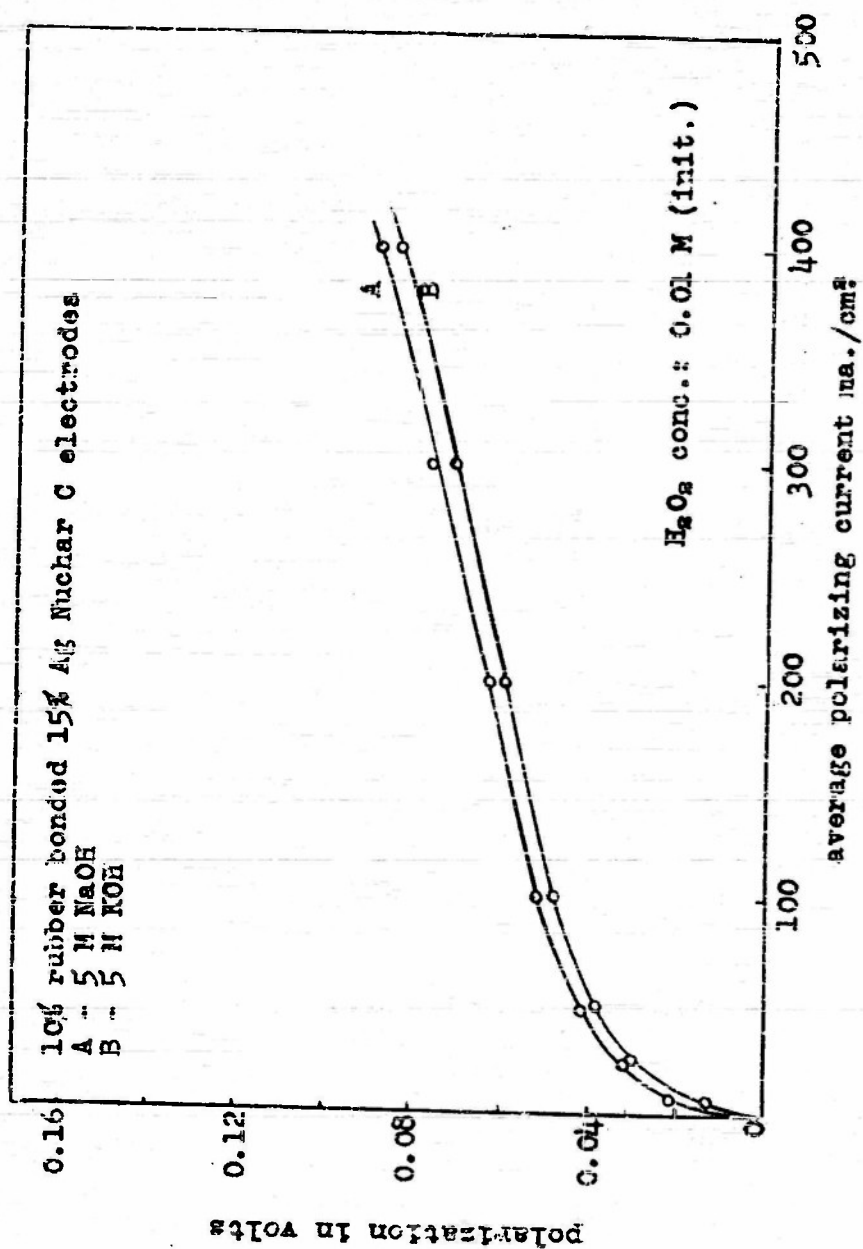
densities for an uncatalyzed carbon, a copper-catalyzed carbon, and a platinum-catalyzed carbon electrodes. The negative potentials for the catalyzed carbons are the result of the peroxide decomposing properties of the catalysts in the carbon since a non-catalyzed carbon reference electrode was used.

c. Cation effects. --The evaluation of possible differences in the behavior of various cations required an electrode stable enough to be used for several determinations in various alkaline electrolytes. While untreated carbons have this stability only in KOH, electrodes prepared in the same manner containing 15% silver deposited by chemical reduction are stable in other basic solutions as well and permit an observation of any differences in the solutions tested. In Figure 35 are shown a comparison of polarization curves in 5 M NaOH and KOH solutions. The polarization in the KOH solution was slightly lower than in the NaOH solution at all current densities.

d. Time dependence. --Measurements indicate that the 15% silver electrodes have low polarizations with little drift at currents of 100 ma./cm.² for periods of 12 hours. The initial polarization always dropped to a stable value within 10 minutes at 200 ma./cm.² as in the case of the non-treated carbons.

4. Metal Oxygen Electrodes

Active carbon has been replaced with iron, cobalt,

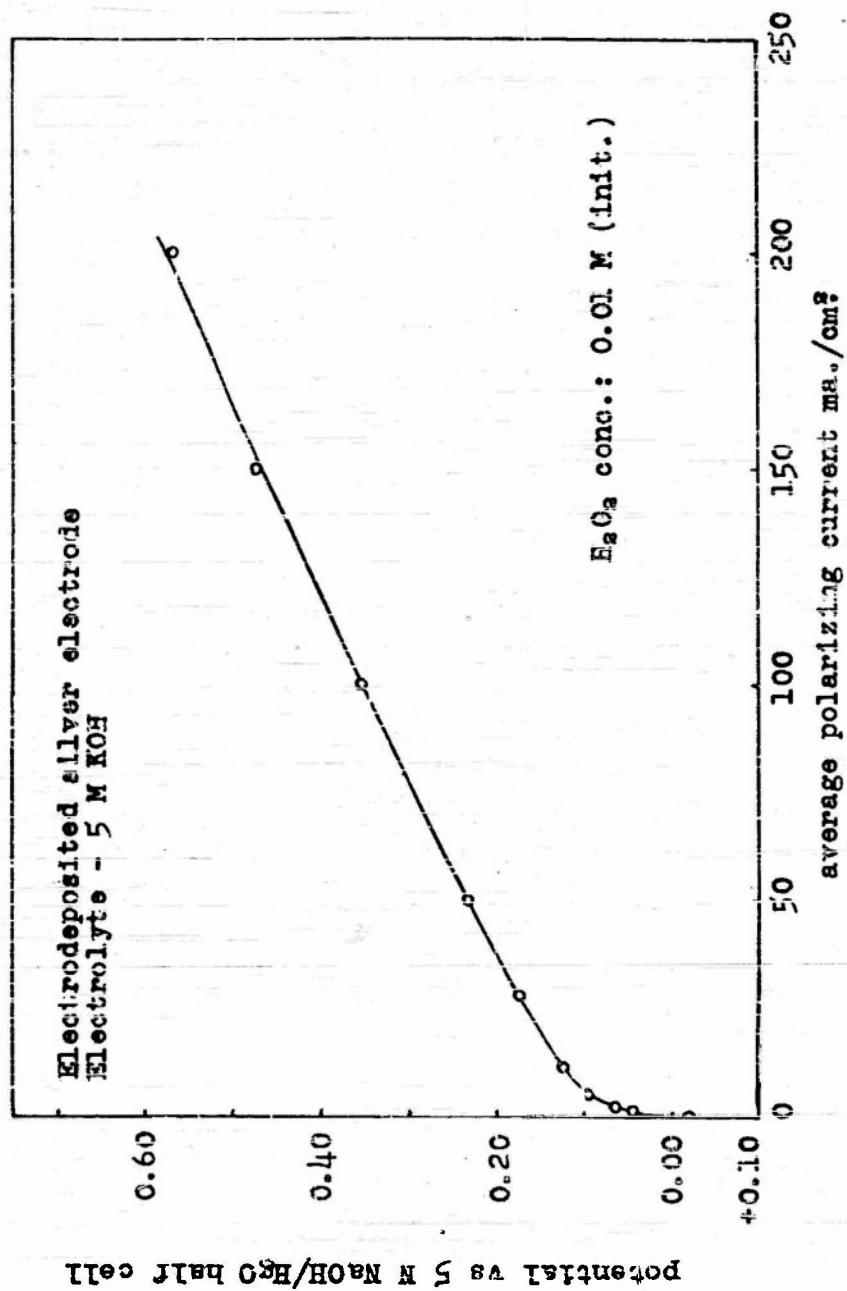


Comparison of Electrolytes for Silver Treated Carbon

Figure 36

nickel, and silver powders as a spray coating on porous graphite. With the metals the proportion of binder was reduced to 2% due to the low specific volume of these materials. Oxygen gas was introduced in the same fashion as with the active carbon electrodes.

The results obtained from all these metals have been unsatisfactory since the polarizations were little better than graphite itself with the exceptions of silver and copper. The copper does not polarize excessively at low currents but dissolves rapidly at higher currents in strongly alkaline solutions. Electrodeposited silver gave the results shown in Figure 37.



Polarization of an Electrodeposited Silver Electrode

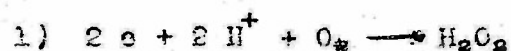
Figure 37

PART IV: DISCUSSION OF EXPERIMENTAL RESULTS

A. The Overall Reaction

1. Modern Theories

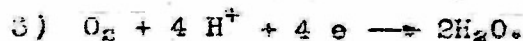
Modern theories of the oxygen electrode postulate the reduction of oxygen in two stages at normal temperatures. The first stage is represented by



and the second by



The overall reaction is



The second step is not electrochemical and does not furnish electrical energy.

2. Causes of Misunderstanding among Original Researchers

Experimental data, amassed during the first 30 years of the twentieth century, on the potential of the oxygen electrode were unsatisfactory and led to the elaboration of conflicting hypotheses. The facts which evoked question were.

a) The potential of the experimental oxygen electrodes does not correspond to the theoretical values expected of the following reactions.

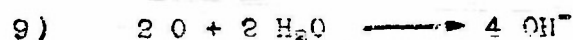
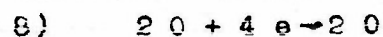
4) Acid media: $O_2 + 4 H^+ + 4 e \rightarrow 2 H_2O$; $E^0 = -1.2229$ v.

5) Neutral media: $O_2 + 4 H^+ (10^{-7} M) + 4 e \rightarrow 2 H_2O$;
 $E = -0.815$ v.

6) Basic media: $O_2 + 2 H_2O + 4 e \rightarrow 4 OH^-$; $E = -0.401$ v.

b) Most potentials of experimental electrodes were not reproducible and had a tendency to wander over long periods of time. Under controlled conditions¹ the e.m.f. of several different metallic electrodes, initially divergent, tended to drift to final, more or less, stable values.

c) A source of much misunderstanding was the belief that oxygen electrodes operated in accordance with the classical mechanism.



Another reason for the confusion was the achievement of Haber² who succeeded in obtaining the theoretical e.m.f. of the O_2 -- H_2 cell using platinum electrodes in molten electrolytes at high temperatures. This result has never been duplicated at low temperatures by numerous experimentalists working in aqueous media. Many vain attempts to obtain the theoretical value for the H_2 -- O_2 cell in aqueous media were based on the ignorance of the

¹H. Bain, Trans. Electrochem. Soc., **76**, 173 (1940).

²F. Haber, Z. Elektrochem., **12**, 415 (1908).

fact that oxygen is first reduced to peroxide.

3. The Peroxide Theory

Abundant evidence^{3,4} from the studies of the corrosion of metals in moist air indicates that the reduction of oxygen is probably always accompanied by the formation of H_2O_2 . Modern researches to this effect have culminated in the papers of J.R. Churchill⁵ who has shown the formation of peroxide to be quite general on metallic surfaces. Those metals which do not exhibit the formation of H_2O_2 are excellent catalysts for its decomposition. The information from corrosion studies led Haber⁶ and independently Lewis⁷ to postulate the reduction of oxygen in two stages via the formation of peroxide.

K. Bornemann⁸ measured the static e.m.f. of the oxygen electrode in acidic peroxide with a platinum electrode. His value of $0.66 \pm .03$ volt is in close agreement with the theoretical value of 0.68 volt calculated.

³Dunstan, Jowett, and Goulding, J. Chem. Soc., 97, 1548 (1905).

⁴M. Traube, Ber., 15, 2434 (1882).

⁵J. Churchill, Trans. Electrochem. Soc., 76, 341 (1939).

⁶F. Haber, Z. anorg. allgem. Chem., 51, 356 (1906).

⁷G. Lewis, J. Am. Chem. Soc., 28, 158 (1906).

⁸K. Bornemann, "Nernst Festschrift," Knapp, Halle, 1912, p. 118.

by Lewis and Randall⁹. In view of the excellent theoretical work of Haber, Lewis and Randall, and the empirical agreement of Bornemann's experiments, it is rather that later workers in the oxygen electrode field did not clearly understand why the theoretical oxygen-water potential was not obtained.

Heyrovsky¹⁰ observed that the reduction of oxygen at the dropping mercury electrode proceeds in two steps with hydrogen peroxide as a postulated intermediate. Later polarographic workers¹¹ agree with him.

Hydrogen peroxide was found to be produced in small amounts at the oxygen electrode of Fischer and Kronig¹² during electrolysis.

Lamb and Elder¹³ showed that catalysts which increase the rate of decomposition of peroxide were desirable as cathodic depolarizers in galvanic cells (e.g. platinum black, iron, pyrophosphate ion, copper salts, and active carbon).

⁹Lewis and Randall, J. Am. Chem. Soc., 36, 1909 (1914).

¹⁰J. Heyrovsky, Trans. Far. Soc., 19, 735 (1924).

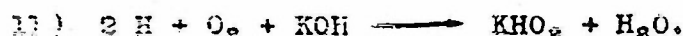
¹¹Kolthoff and Miller, J. Am. Chem. Soc., 63 (1941).

¹²Fischer and Kronig, Z. anorg. allgem. Chem., 135, 169 (1924).

¹³Lamb and Elder, J. Am. Chem. Soc., 53, 162 (1931).

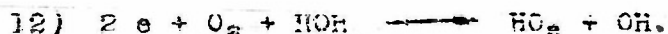
J.R. Churchill,⁵ while investigating the corrosion of metals, observed that the rate of production of peroxide in solutions of varying pH was increased by making the metals more cathodic by the passage of very small currents. Mass action effects were observed, e.g., it was found that in the case of aerated aluminum wire immersed in H_2SO_4 , the rate of production of peroxide was inhibited as the concentration of peroxide was increased.

Interest in the cheap commercial production of H_2O_2 led E. Berl¹⁴ to demonstrate that oxygen was converted to H_2O_2 at the activated carbon cathode immersed in KOH with current efficiencies better than 90%. Berl proposed the following overall reaction to account for the observed facts:



4. The peroxide Mechanism in Basic Solution

The final proof of the nature of the oxygen electrode came with the extensive measurements of W.G. Berl¹⁵. He assumed the reaction in basic solution to be



Since the electrode should behave in accordance with the Nernst relation for the assumed reaction, i.e.

¹⁴ E. Berl, Trans. Electrochem. Soc., 76, 359 (1939).

¹⁵ W. Berl, Trans. Electrochem. Soc., 93, 265 (1943).

$$13) \quad E = E^{\circ} - \frac{RT}{nF} \ln \frac{(a_{OH^-})(a_{HO_2^-})}{(a_{H_2O})(p_{O_2})}$$

Berl proceeded to test the behavior of the potential of the electrode under varying activities of OH^- and HO_2^- ion concentrations. His experimental results have been plotted in Figure 3 in Part I and show the linear relationship between the potential and the logarithm of the HO_2^- ion concentration which must exist if the hypothesis is correct and the activity coefficient is assumed constant. The non-linear portions of the curve are in the regions where the HO_2^- ion concentration is appreciably depleted by association with the hydrogen ion. The curvature becomes apparent at concentration ratios of peroxide to hydroxide of 0.40. This effect is apparent even at a pH of 14 or greater and results from the similar dissociation properties of peroxide and water.

The differentiation of the Nernst equation with respect to the logarithm of the reactants yields the slopes

$$\frac{\partial E}{\partial \log a_{HO_2^-}} = \frac{\partial E}{\partial \log a_{OH^-}} = -\frac{2.3RT}{2F} = -0.03$$

and

$$\frac{\partial E}{\partial \log P_{O_2}} = \frac{2.3RT}{2F} = 0.03.$$

On the other hand the classical overall reaction,



yields the slopes

$$\frac{\partial E}{\partial \log a_{HO_2^-}} = 0$$

$$\frac{\partial E}{\partial \log a_{OH^-}} = -0.06$$

$$\frac{\partial E}{\partial \log P_{O_2}} = 0.015.$$

Berl obtained the value

$$\partial E / \partial \log a_{HO_2^-} = -0.0309$$

as the average for eight experimental curves from 0.10 to 11 M KOH; and

$$\partial E / \partial \log a_{OH^-} = -0.026.$$

This latter value is subject to errors in calculation since Berl did not have the activity coefficients of the KOH at high concentrations and assumed the activity of water constant in equation (13).

Kordesch and Martinola¹⁶ reported the value

$$\frac{\partial E}{\partial \log P_{O_2}} = 0.0292.$$

This value is subject to uncertainty resulting from the lack of a peroxide control. The excellent agreement of the slopes with the theoretical requirements of the Nernst equation constitutes an additional proof of the peroxide theory.

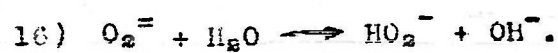
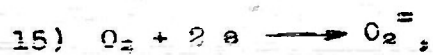
¹⁶ Kordesch and Martinola, Monatsh., 84, 39 (1953).

¹⁷ T. Hoar, Proc. Roy. Soc. (London), A, 142 628 (1933).

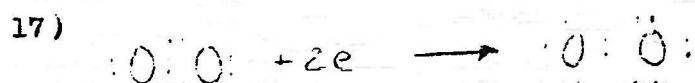
B. The Mechanism of the Reaction

1. The Mechanism of W.G. Berl¹⁴

The mechanism proposed by Berl to explain the reduction of oxygen to perhydroxide ion is as follows, Two steps are involved in the reaction, i.e.



A proton exchange between a water molecule and an oxygen molecule takes place in the second step. Two electrons are transferred simultaneously or prior to the proton exchange, and an oxygen molecule with a complete octet is formed



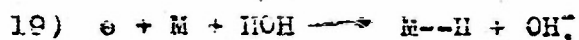
Neither of these steps requires the fracture of the oxygen O--O bond. Any further reduction to water, however, would require the rupture of the O--O bond in the peroxide molecule.

2. The Bratzler Mechanism

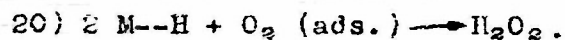
K. Bratzler¹⁸ proposed that nascent hydrogen is

¹⁸K. Bratzler, Z. Elektrochem., 54, 81 (1950).

formed not only in NH_4Cl solutions, but in strongly basic solutions of NaOH . The proton is obtained from water thus:



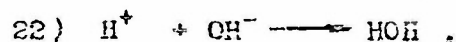
where M is a site, the nature of which will be discussed later. The nascent hydrogen then reacts with the adsorbed oxygen.



This mechanism is in accord with the mechanism of W.G. Ber¹⁴ in that it also does not require the fracture of the O--O bond.

3. Anodic Mechanism of Hickling and Wilson

The reaction of Hickling and Wilson¹⁹ for the oxidation of aqueous peroxide at a microelectrode in basic solution was postulated to be the reverse of reaction (12), i.e.



These reactions take place more rapidly than the reduction of the hydroxyl ion and, in general, the rate of the reaction was found to be governed by the diffusion of the HO_2^- ions.

¹Hickling and Wilson, Trans. Electrochem. Soc., 98, 425 (1951).

4. The Work of Taube on Peroxide with O^{18}

Taube et al.^{20, 21} who have studied the decomposition of hydrogen peroxide using O^{18} as a tracer, find that exchange between systems involving the peroxide O--O bonds and water occurs only slightly if at all in acid solution. According to these workers an oxidizing agent functioning by the removal of electrons strengthens the O--O bond. Thus it is probable that in the chemical oxidation of peroxide the O--O bond is never broken. Generalization of this fact can be extended to the reversible oxygen electrode, i.e. the oxygen molecule is reduced to peroxide without rupture of the O--O bond.

5. Discussion of Mechanisms

The Bratzler mechanism¹⁸ cannot be discounted because at finite overvoltages even in basic solution a definite quantity of hydrogen must be liberated, but the contribution of this hydrogen to the current may be small and restricted to zones where the oxygen pressure is low. The Berl mechanism, on the other hand, receives support from the reverse reaction of Hickling and Wilson¹⁹ since in the migration of the HO_2 ion to the anode, it should be the negative oxygen side of the ion which approaches the positive site. The removal of electrons and proton

²⁰ Cahill and Taube, J. Am. Chem. Soc., 74, 2312 (1952).

²¹ Hunt and Taube, ibid., 74, 5999 (1952).

may be almost simultaneous in a push-pull play by the anode site for electrons on one hand and OH^- ions for the protons on the other. The oxygen molecule is left in a physisorbed state in equilibrium with the oxygen dissolved in the surrounding solution and/or gas phase oxygen.

c. The Role of the Electrode

The active material in an oxygen electrode serves to deliver the oxygen to the active sites and supply the electrons required for the reaction.

The ideal electrode would possess infinite adsorptive power for oxygen and at the same time would have a uniformly pervasive system of macro and micro pores to deliver the oxygen efficiently to the reaction zone. Electrical resistivity would be zero. In order to obtain an unlimited number of reaction sites the surface area would approach infinity. In this connection the three phase zone is discussed below.

1. The Three Phase Zone

The low solubility of oxygen in aqueous solutions limits severely the amount of oxygen that can diffuse to the region of the carbon at which some form of adsorbed oxygen is electrochemically converted to peroxide. In view of the relatively small polarization even at high current densities, it is convenient to postulate the existence of an ill-defined three phase zone involving a gas phase, solution, and solid.

The work of Bratsler¹⁶ supports the hypothesis that the three phase region is a function of the surface area, and indirectly, the pore structure by obtaining lower polarizations with increased subdivision of active carbon. Binders tend to deplete the amount of three phase zone by occlusion of the pores and surface. Wetproofers in excessive amounts likewise are deficient although they are designed to enhance the amount of three phase zone when present in the proper amount.

The porosity of the carbon permits the oxygen to diffuse to the regions where the electrochemical reaction reduces the concentration of adsorbed oxygen. The surface mobility of physically adsorbed oxygen may also contribute to the transport of oxygen to the sites of the electrochemical reaction in the phase zone. A minimum oxygen pressure and surface tension prevents the adsorption of the electrolytes into the active zone by capillary action. In this connection oxygen diluted with nitrogen should tend to prevent wetting in oxygen starved zones according to Weiss and Jaffe.²² It is probable that fluctuating electrocapillarity and oxygen pressure cause rapid changes in the three phase zone boundaries.

Powdered metals and graphite differ from active carbon in their electrode properties because of surface area among other factors (catalytic sites, inertness etc.).

²² Weiss and Jaffe, Trans. Electrochem. Soc., 93, 128 (1948).

The active carbon particles are unique in that they possess higher surface areas (from 2-2000 $M^2/g.$). The contact zone between the internal pore structure, where high oxygen concentration can exist, and the external surface, bathed by electrolyte, may be the region where the majority of electrochemical reaction occurs, i.e. the three phase zone. Metals and graphite might not possess such a region to any appreciable extent.

The practice of wetproofing an electrode material is designed to increase the three phase zone. Often the wet-proofer may also function as the binder.

2. Binders

The purpose of a binder is to bend the active carbon material into a form suitable for use. If the active material is formed in a massive state, there is no need for a binder.

The ideal binder would have certain properties which are only partially fulfilled by actual materials. These are:

- (1) A low electrical resistance.
- (2) Only a small amount should be required to form a sufficiently rigid mass.
- (3) It should add to rather than detract from the porosity of the bonded product.
- (4) It should be chemically inert to both electrolyte and oxygen.
- (5) It should possess inherent optimum wetproofing properties in its structure.

The amount of binder most commonly employed in the present work was 5% by weight of carbon for highly activated 200 mesh or finer materials. This amount was chosen because it is the minimum amount which gives good adherence and sufficient wetproofing. Higher proportions of binder give more adherent coatings but result in higher electrical resistance, decreased three phase area, and the reduction of the porous structure of the electrode. As a general rule, the amount of binder should be proportional to the specific volume of the active material.

As has been described in Part III, polyethylene, rubber, polystyrene, and ethylcellulose have been tested as binders.

The properties of polyethylene are somewhat different from most other binding materials in that it is soluble in aromatic organic solvents when hot but forms a suspension of fine particles when cooled to room

temperature. Carbon layers prepared with this material are highly porous due to the interspersation of the particles of plastic. An electron micrograph has shown that the carbon particles are only partially covered with the plastic which permits a larger three phase area to exist. The adherence of polyethylene bonded materials is not good because of the particle-like nature rather than film-like nature of the plastic as it is used. The excellent water and alkali repellent properties of this material are a direct consequence of its hydrocarbon structure and are comparable with paraffin (a commonly employed wetproofener). The electrical resistance of the polyethylene carbons are somewhat higher than those bonded with other materials due to the manner in which the plastic particles separate the carbon particles.

Pure crepe rubber is a **very** satisfactory binding agent from several standpoints. It forms more adherent coatings than the polyethylene from the same amount of material employed, and the layers are somewhat flexible. The material does not have quite the degree of wetproofing action possessed by the previously mentioned material but it is quite stable to alkali at all concentrations. A small amount of polyethylene or paraffin incorporated in the mixture should augment the hydrophobic characteristics.

Polystyrene shows excellent resistance to strong alkalies and gives quite firm layers of active carbon.

The polarization seems to be higher for this material compared to the other binders when used in the same proportions. This is possibly due to some property of the polymer which causes it to plug the pores of the carbon or seat the particles more completely.

Ethylcellulose was found to be suitable for static measurements. In the case of high currents, measurements could only be made for short periods of time because the alkali begins to hydrolyze the plastic and the carbon layer was soon destroyed.

3. The Electrochemical Sites

Two types of sites are probably available with active carbon for the electrochemical reduction of oxygen to peroxide: chemi-adsorbed oxygen and physi-adsorbed oxygen. The co-existence of both chemi- and physi-adsorbed oxygen in carbon is well substantiated by various types of gas-adsorption studies. The electrochemical evidence favors the hypothesis that the physi-adsorbed oxygen is the species involved directly in the formation of the peroxide. This evidence is as follows:

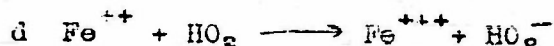
1. The relatively small activation polarization associated with the oxygen cathode is usually more characteristic of a physical rate process.
2. The relatively small temperature coefficient of the cathodic polarization implies a physical activation.
3. The fact that the peroxide is formed implies that the O-O bond is not broken.

Further information concerning the nature of the sites for the electrochemical reaction on active carbon should be forthcoming from current work involving the correlation of gas adsorption data with polarization measurements and the use of oxygen-18 in tracer and fractionation studies.

D. Catalytic Decomposition of Peroxide

1. Mechanism of Peroxide Decomposition

Barb, Baxendale, George, and Hargrave²⁴ have presented experimental evidence which supports most of the Haber-Weiss²⁵ mechanism for the simple iron catalyzed decomposition of peroxide in acid solution. This mechanism, modified to fit their kinetic studies more accurately, is as follows.



The reaction 25a results in one reduced oxygen atom. The OH free radical may react along the alternative routes 25b and 25c, the rates of which depend on the concentration of the Fe^{++} ion. Oxygen is formed through the two reactions 25c and 25e with 25d a competing path for the radical HO_2 . When the ratio of the ferric ion to ferrous ion remains constant, two moles of water and one mole of oxygen are produced largely through 25a, 25c, and 25e.

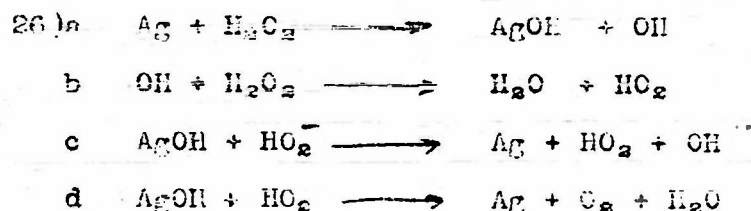
²⁴ Barb, Baxendale, George, and Hargrove, Trans. Far. Soc., **47**, 462 (1951).

²⁵ Haber and Weiss, Proc. Roy. Soc., **A147**, 332 (1934).

Since the simple chemical decomposition of peroxide yields two molecules of water and one molecule of oxygen, the balance of oxidation and reduction processes (auto redox) is equal. At an electrode, unless an auto redox reaction is unbalanced, the net process yields no electrochemical energy.

It is possible to generalize the mechanism 25 to other redox systems. The most interesting of these will be those characterized by a negative free energy change and a low activation energy in each reaction.

The mechanism is applicable to heterogeneous as well as homogeneous systems. In particular the 15% silver catalyzed carbon electrode surface in basic solution may behave thus:



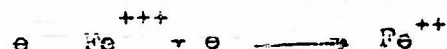
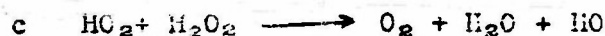
In any event the silver acts as an oxidation reduction catalyst for the chemical decomposition of the peroxide.

2. Catalytic Electrochemical Reduction of Peroxide

The catalytic reduction of peroxide would make available the electrochemical energy of the peroxide. The report of Weisz and Jaffe²² that electrochemical reduction of peroxide does not occur in basic solution was based on graphite and mercury surfaces and not on surfaces which would catalyze the reduction of peroxide. The iron catalyzed reduction of peroxide at the mercury

micro electrode in 0.25 M H_2SO_4 obeys a Haler —
 Weiss²⁵ mechanism according to Kolthoff and Parry²⁶

i.e.,



Peroxide is converted to a reduced hydroxide ion and an OH radical in 27a. The radical may be reduced to hydroxide through 27d or it may form HO_2 and thereby O_2 through 27b and 27c. The electrochemical step is 27e. Since there is a predominance of reaction 27a and 27d over the oxygen forming reactions 27b and 27c, some electrochemical reduction occurs.

It is likely than an excess of oxidizing or reducing action over the other must always occur because catalysts do not exist which have equal free energies in the reduced and oxidized states unless the concentration ratio of the oxidation states has been previously adjusted. In a closed electrochemical circuit this state of conditions will afford electrochemical energy. Therefore, coincident with the Berl process¹⁸, there may be electrochemical reduction at the dynamic oxygen cathode in basic

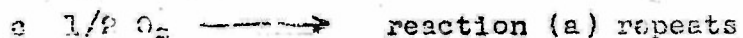
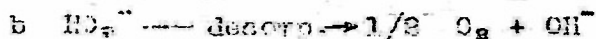
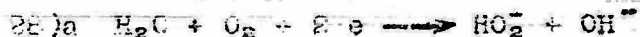
²⁶ Kolthoff and Parry, J. Am. Chem. Soc., **73**, 3718 (1951).

solution even in the presence of excess oxygen. Such a process would result in an increasing reduction potential with increasing peroxide concentration which is a response contrary to the Berl mechanism.

3. Catalyzed Carbon Electrodes

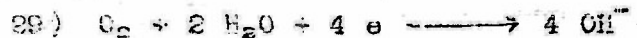
a. Effect on polarization. --One of the simplest explanations for the decreased polarization associated with the CuO and Ag containing active carbon cathodes is as follows:

Both CuO and Ag are good catalysts for the catalytic decomposition of peroxide in basic solution with the silver perhaps somewhat better than the CuO. The oxygen liberated through the decomposition of the peroxide becomes available for electrochemical reduction in the third stage of the processes shown below.



These processes may recycle until the oxygen is entirely reduced to hydroxide ions rather than peroxide ions.

This will result in the transfer of the same number of electrons per oxygen molecule as in the direct reduction of oxygen to hydroxide ions, i.e.



The decrease in the peroxide concentration at the electrode surface also reduces the concentration polarization to a major extent. The unsatisfactory behavior of the copper treated carbon may be explained

on the basis of the solution of the copper in the electrolyte.

Electrodes in which the peroxide decomposing catalyst has been incorporated by electrodeposition are not as satisfactory as the impregnated type. Electrodes which have been externally platinized by electrodeposition show lower polarization but do not slow the penetration of the electrolyte in NaOH at high current densities. The external layer of platinum must be quite thin, as an excess will block off too much of the active three phase area of the electrode.

b. Penetration of electrolyte. --The carbons containing CoO and Ag do not show the rapid penetration of electrolyte and destruction of active carbon films common to non-treated carbons when used in NaOH. This phenomenon seems to be connected in some way to the presence of the peroxide which is formed in the electrode process.

It is known that the sodium salts of the peroxide formed are less soluble and more unstable than the corresponding potassium ones. Sodium peroxide may precipitate within the active carbon. The possibility also exists that the destruction of the carbon is brought about through the release of large oxygen bubbles when the concentration of the sodium peroxide in the pores of the carbon becomes high enough. The presence of peroxide decomposing catalysts in the carbon, or an increase in the temperature of the electrolyte would decrease the

damage of the electrodes by effecting a uniform decomposition of the peroxide as it is formed.

The peroxide decomposing catalysts are more suitable for this purpose since a high temperature might soften the binding material.

E. Polarization

1. Concentration Polarization

a. Diffusion limited oxygen.--The major source of polarization originates in concentration polarization which often masks the activation polarization unless precautions are taken to minimize it. Weisz and Jaffe²² have shown that the diffusion limited flow of oxygen was rate determining in their zinc-activated carbon air cells. For a rectangular block of thickness x , the perpendicular diffusion of oxygen following Fick's law may be written approximately as

$$\frac{dn_{O_2}}{dt} = D_1 \frac{A}{x} [(a_{O_2})_2 - (a_{O_2})_1]$$

where $\frac{dn_{O_2}}{dt}$ is the rate of oxygen flow perpendicular to the face of the block, D_1 is the diffusion coefficient of the oxygen in moles $\text{cm}^{-2} \text{ atm}^{-1} \text{ sec}^{-1}$, A is the area of the block, $(a_{O_2})_2$ is the activity of oxygen on the air side of the block, and $(a_{O_2})_1$ is the activity of oxygen on the electrolyte side of the block.

If each oxygen molecule is ultimately reduced to water, then the total equivalents of current, $\frac{i}{F}$, is divided by 4 is equal to the oxygen flow.

$$31) \frac{dN_{O_2}}{dt} = \frac{i}{4F} = D_2 \frac{A}{X} [(a_{O_2})_2 - (a_{O_2})_1]$$

b. A mathematical interpretation. --The analysis of concentration polarization has led to the mathematical study presented below. This development is based on the peroxide mechanism.

Under reversible conditions, equation (13) is applicable at the oxygen electrode.

$$32) E_{rev} = E^0 - 0.03 \log \frac{(a_{OH^-})(a_{H_2O_2^-})}{(a_{O_2})(a_{H_2O})}$$

where E^0 is the standard potential of the electrode, E_{rev} is the reversible half-cell potential, and a is the activity of the species in subscripts at the electrode surface and in the bulk of the solution. Under irreversible cathodic conditions, it is assumed that

$$(33) E_{ir} = E^0 - 0.03 \log \frac{(a_{OH^-})_{ir} (a_{H_2O_2^-})_{ir}}{(a_{O_2})_{ir} (a_{H_2O})_{ir}}$$

where the subscripts *ir* refer to the irreversible dynamic conditions at the electrode surface.

Activation polarization is not considered in equation (33).

According to equation (31), the activity of oxygen at the electrode-electrolyte interface is given thus:

$$(34) \quad (a_{O_2})_{ir} = a_{O_2} - \frac{I \lambda}{n D_1 F} = a_{O_2} - k_1 I$$

where *n* represents the average number of electrons taken up by all oxygen species and varies between 2 and 4.

I is the current density, k_1 is $\frac{\lambda}{n D_1 F}$, and a_{O_2} is the activity of oxygen at the interface in the absence of polarizing current. The quantity $(a_{O_2})_{ir}$ is the same as a_{O_2} in equation (31).

In the steady state at any given current density

$$(35) \quad \frac{d(m_{H_2O_2})}{dt} = \frac{I}{2F} - K(a_{H_2O_2})_{ir} - \frac{D_2}{\delta} [(a_{H_2O_2})_{ir} - (a_{H_2O_2})] = 0$$

where $\frac{d(m_{H_2O_2})}{dt}$ is the rate of change of peroxide ion per cm² at the interface with time, *K* is a first order rate constant for the decomposition of peroxide and is specific for any given solution and the heterogeneous catalysts of the electrode. *D*₂ is the diffusion coefficient of the peroxide, and *δ* is the effective thickness of the diffusion layer. Electrolytic transport has been neglected

It is assumed that oxygen moves only by diffusion. Under convection an additional pressure gradient term would be added.

in equation (35); hence this equation is limited to conditions for which the transference number of the perhydroxide ion at the cathode interface is very small. If this equation is solved for $(a_{HO_2^-})_{ir}$, there is obtained

$$36) \quad (a_{HO_2^-})_{ir} = \frac{D_2(a_{HO_2^-})}{\delta(K + \frac{D_2}{\delta})} + \frac{I}{2F(K + \frac{D_2}{\delta})}$$

or

$$37) \quad (a_{HO_2^-})_{ir} = k_2 I + k_3(a_{HO_2^-})$$

$$\text{where } k_2 = \frac{1}{2F(K + \frac{D_2}{\delta})} \quad \text{and } k_3 = \frac{D_2}{\delta(K + \frac{D_2}{\delta})} = \frac{1}{(\frac{\delta K}{D_2} + 1)}$$

The equation for OH^- ions in the steady state is

$$38) \quad \frac{d(n_{OH^-})}{dt} = \frac{I}{2F} + K(a_{HO_2^-})_{ir} - \frac{D_3}{\delta} [(a_{OH^-})_{ir} - (a_{OH^-})] - \frac{I\epsilon}{F} = 0$$

where $\frac{d(n_{OH^-})}{dt}$ is the rate of change of the OH^- ion per cm.² at the interface with time, D_3 is the diffusion coefficient for the OH^- ion, and ϵ is the transference number of the OH^- ions. The term $K(a_{HO_2^-})_{ir}$ arises because each HO_2^- ion decomposes to one OH^- ion and $1/2 O_2$. Although the term K depends on the OH^- ion concentration, this dependence is neglected for the purpose of simplification on the basis that $(a_{OH^-})_{ir}$ does not differ too much from (a_{OH^-}) . If equation (36) is solved for $(a_{HO_2^-})_{ir}$,

$$39) (a_{OH^-})_{ir} = \frac{I\delta(1-2\epsilon)}{2D_2F} + \frac{\delta K}{D_2} (a_{OH^-})_{ir} + (a_{OH^-})$$

If equation (36) is used for eliminating $(a_{HO_2^-})_{ir}$

$$40) (a_{OH^-})_{ir} = \frac{I\delta(1-2\epsilon)}{2D_2F} + \frac{I\delta K}{2D_2F(K + D_2/\delta)} + \frac{D_2 a_{HO_2^-}}{D_2(K + D_2/\delta)} + a_{OH^-}$$

If the activity of the peroxide in the bulk of the solution is small, which is generally the case

$$41) (a_{OH^-})_{ir} \cong \frac{I\delta}{2D_2F} \left[1 - 2\epsilon + \frac{1}{(1 + D_2/\delta K)} \right]$$

and

$$42) (a_{OH^-})_{ir} = k_0 I + (a_{OH^-})$$

where

$$k_0 = \frac{\delta}{2D_2F} \left[1 - 2\epsilon + \frac{1}{(1 + D_2/\delta K)} \right]$$

The activity of the water at the electrode interface may also differ appreciably from that in the bulk of the solution because of differences in the concentration of the cation (potassium or sodium) as well as the anions (hydroxide and perhydroxide). This variation in the activity of water may be calculated by means of the Gibbs -Duhem equation which in differential form is

$$43) \quad (n_{H_2O}) d \ln(a_{H_2O}) + (n_+) d \ln(a_+) + (n_{OH^-}) d \ln(a_{OH^-}) \\ + (n_{HO_2^-}) d \ln(a_{HO_2^-}) = 0,$$

where n is the number of moles of the species indicated by the particular subscript and a_+ is the activity of the cation ion. The limitation has already been imposed that the ratio of perhydroxide to hydroxide be small compared to unity (neglect of electrolyte transport of perhydroxide ions). Hence, the concentration of the cation is substantially the same as the hydroxide in concentration.

On this basis, $n_+ = n_{OH^-}$ and $(a_{\pm})^2 = (a_+) (a_{OH^-})$

where a_{\pm} is the mean activity for the base.

In the present calculation, the mean activity a_{\pm} for the base will be assumed equal to the activity of the hydroxide ion. This approximation is not drastic in as much as there is considerable self compensation involved. The integrated form of equation (43) is then

$$44) \quad \ln \left[\frac{(a_{H_2O})_{ir}}{(a_{H_2O})} \right] = - \int_{(a_{OH^-})}^{(a_{OH^-})_{ir}} \frac{(2 n_{OH^-})}{(n_{H_2O})} d \ln (a_{OH^-}) \\ - \int_{(a_{HO_2^-})}^{(a_{HO_2^-})_{ir}} \frac{(n_{HO_2^-})}{(n_{H_2O})} d \ln (a_{HO_2^-})$$

or
45)

$$(a_{H_2O})_{ir} = (a_{H_2O}) \exp - \left[\int_{(a_{OH^-})}^{(a_{OH^-})_{ir}} \frac{(2 n_{OH^-})}{(n_{H_2O})} d \ln (a_{OH^-}) \right. \\ \left. - \int_{(a_{HO_2^-})}^{(a_{HO_2^-})_{ir}} \frac{(n_{HO_2^-})}{(n_{H_2O})} d \ln (a_{HO_2^-}) \right]$$

The limits $(a_{OH^-})_{ir}$ and $(a_{HO_2^-})_{ir}$ may be established from equations (42) and (37) respectively.

The polarization may be defined thus:

$$(47) \quad \eta = E_{\text{rev.}} - E_{\text{ir.}}$$

where η is the concentration polarization. Substituting for $E_{\text{ir.}}$ and $E_{\text{rev.}}$ one obtains

$$(48) \quad \eta = 0.03 \left[\log \frac{(a_{\text{OH}^-})_{\text{ir.}}}{(a_{\text{OH}^-})} + \log \frac{(a_{\text{H}_2\text{O}_2})_{\text{ir.}}}{(a_{\text{H}_2\text{O}_2})} \right. \\ \left. - \log \frac{(a_{\text{O}_2})_{\text{ir.}}}{(a_{\text{O}_2})} - \log \frac{(a_{\text{H}_2\text{O}})_{\text{ir.}}}{(a_{\text{H}_2\text{O}})} \right]$$

Using (34), (37), (42), and (45), one obtains

$$(49) \quad \eta = 0.03 \left[\log \frac{k_4 I + (a_{\text{OH}^-})}{(a_{\text{OH}^-})} + \log \frac{k_2 I + k_3 (a_{\text{H}_2\text{O}_2})}{(a_{\text{H}_2\text{O}_2})} \right. \\ \left. - \log \frac{(a_{\text{O}_2}) - k_1 I}{(a_{\text{O}_2})} - \log \frac{(a_{\text{H}_2\text{O}})_{\text{ir.}}}{(a_{\text{H}_2\text{O}})} \right]$$

or

$$(50) \quad \eta = 0.03 \left[\log \left(1 + \frac{k_4 I}{a_{\text{OH}^-}} \right) + \log \left(k_3 + \frac{k_2 I}{a_{\text{H}_2\text{O}_2}} \right) \right. \\ \left. - \log \left(1 - \frac{k_1 I}{a_{\text{O}_2}} \right) - \log \frac{(a_{\text{H}_2\text{O}})_{\text{ir.}}}{(a_{\text{H}_2\text{O}})} \right]$$

When the current is zero, the polarization is not zero but approximately $0.03 \log k_2$, which is $0.03 \log \left[\frac{k_4}{k_3} + 1 \right]$ and negative. The significance of this negative polarization is that the electrode causes the decomposition of peroxide which results in a potential less than that predicted thermodynamically on the basis of the activities in the bulk phase.

In the region where

$$51) \quad k_4 \frac{I}{(a_{OH^-})} \ll 1 \quad \left[\text{i.e., } \frac{(a_{OH^-})_{ir}}{(a_{OH^-})} \approx 1 \right]$$

$$52) \quad \frac{k_2}{k_3} \frac{I}{(a_{HO_2^-})} \ll 1 \quad \left[\text{i.e., } \frac{(a_{HO_2^-})_{ir}}{(a_{HO_2^-})} \approx 1 \right]$$

and

$$53) \quad k_1 \frac{I}{(a_{O_2})} \ll 1 \quad \left[\text{i.e., } \frac{(a_{O_2})_{ir}}{(a_{O_2})} \approx 1 \right],$$

the expanding of the logarithmic terms and the discarding all terms above powers of one are valid.

Then,

$$54) \quad \eta = 0.03 \left[\frac{k_4 I}{2.3 (a_{OH^-})} + \log k_3 + \frac{k_2 I}{2.3 k_3 (a_{HO_2^-})} + \frac{k_1 I}{2.3 (a_{O_2})} + \int_{(a_{OH^-})}^{\frac{k_4 I + (a_{OH^-})}{n_{H_2O}}} d \log (a_{OH^-}) + \int_{(a_{HO_2^-})}^{\frac{k_2 I + k_3 (a_{HO_2^-})}{n_{H_2O}}} d \log (a_{HO_2^-}) \right]$$

If the latter equation is differentiated with respect to I , one obtains the slope for small values of I .

$$55) \frac{d\eta}{dI} = 0.013 \left[\frac{k_4}{(a_{OH^-})} + \frac{k_2}{k_3(a_{HO_2^-})} + \frac{k_1}{(a_{O_2})} + \frac{2(n_{OH^-})k_4}{(n_{H_2O})(a_{OH^-})} + \frac{(n_{HO_2^-})k_2}{(n_{H_2O})k_3(a_{HO_2^-})} \right]$$

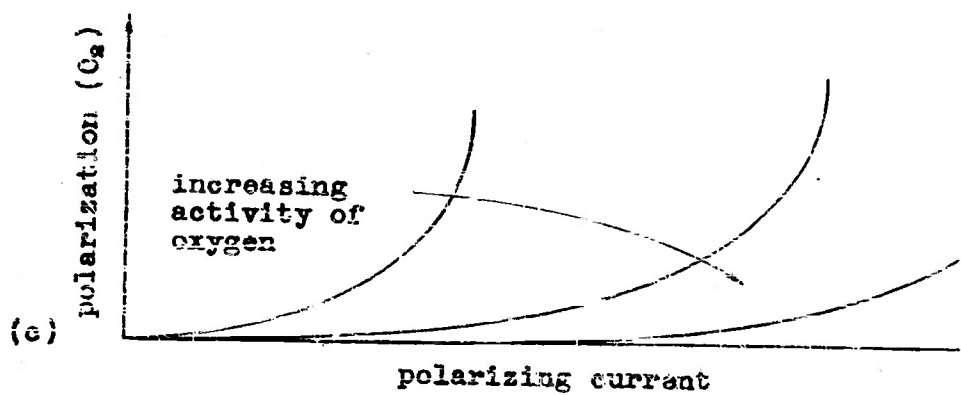
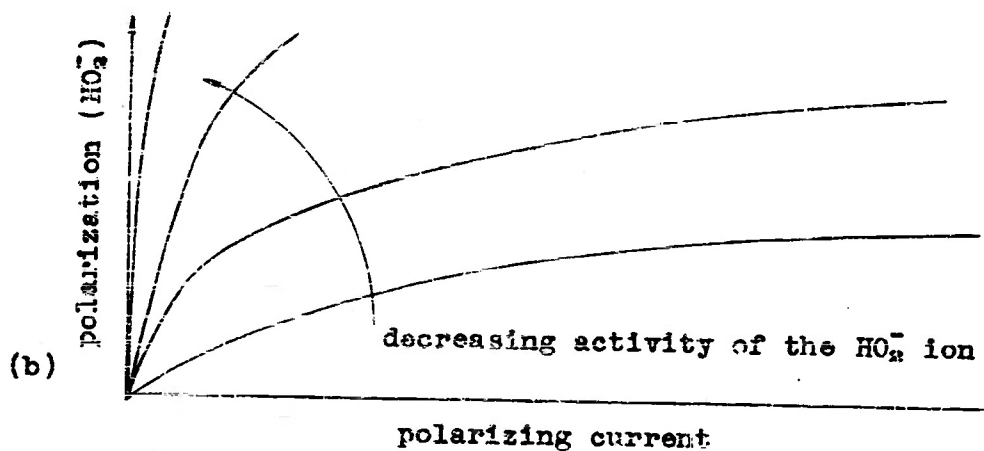
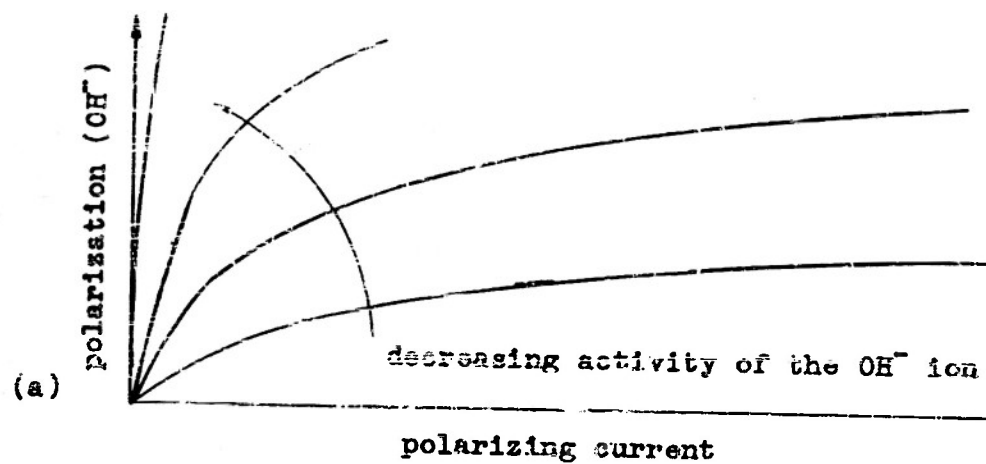
$$56) \frac{d\eta}{dI} = 0.013 \left[\frac{k_4}{(a_{OH^-})} \left(\frac{n_{OH^-}}{n_{H_2O}} + 1 \right) + \frac{k_2}{k_3(a_{HO_2^-})} \left(\frac{n_{HO_2^-}}{n_{H_2O}} + 1 \right) + \frac{k_1}{(a_{O_2})} \right]$$

In concentration ranges where the number of moles of water is large and $(a_{H_2O})_r \approx (a_{H_2O})$ equation (56) reduces to

$$57) \frac{d\eta}{dI} \approx 0.013 \left[\frac{k_4}{(a_{OH^-})} + \frac{k_2}{k_3(a_{HO_2^-})} + \frac{k_1}{(a_{O_2})} \right]$$

The limiting slopes as the current goes to zero are, therefore, inversely dependent on the activities of OH^- , HO_2^- , and the oxygen provided the assumptions concerning the activities and diffusion theory previously mentioned are valid.

If each term of (50) is plotted vs. I on the assumption that all other terms are either constant or negligibly small and the activity of water is constant, one obtains the curves in Figure 38. The curves of η vs. I indicating the hydroxide and peroxide concentration dependence flatten logarithmically. Curves of η vs. I for variable oxygen activity exhibit the rapid upward climb characteristic of diffusion-limited polarographic curves while the regions of low current density are flat. The rapid vertical upsweeps are asymptotic at values of



Curves of the Components of Concentration Polarization

Figure 38

I such that

$$58) \left[1 - \frac{k_1 I}{(a_{O_2})} \right] \rightarrow 0$$

or

$$59) I_{lim} = (a_{O_2})/k_1$$

where I_{lim} represents the limiting current for any given (a_{O_2}) . The quantity k_1 should be a constant for a given electrode-electrolyte system.

The curves of η vs. I for the integral function in equation (50) are roughly proportional to the current density over moderate current density and activity ranges.

c. Comparison with the data. --In equation (50) the second term may be written as the difference of two logarithms:

$$\log (k_3 a_{O_2} + k_2 I) - \log (a_{HO_2^-})$$

If the polarization due to all other terms is assumed an invariant, A, at constant current density, the polarization may be written thus:

$$60) \eta = 0.03 \left[A + \log [k_3 (a_{HO_2^-}) + k_2 I] - \log (a_{HO_2^-}) \right]$$

Differentiating η with respect to $\log(a_{HO_2^-})$ one obtains

$$61) \frac{d\eta}{d \log (a_{HO_2^-})} = -0.03 \left[\frac{1}{1 + \frac{k_2 (a_{HO_2^-})}{k_3 I}} \right]$$

In the range where $(a_{HO_2^-})$ is small and I large, the slope $\left[d\eta / d \log a_{HO_2^-} \right]$

should be -0.03 at constant current density. When the data of Figure 27 are plotted on semilogarithmic axes (Figure 28), a straight line results for peroxide ion concentrations below approximately 0.4 M. Deviation from linearity occurs at higher concentrations. The slope is -0.027 rather than -0.03 . This may be interpreted as due to the neglect of other peroxide-dependent terms, the presence of other current yielding processes in addition to the Berl process, or an increasing adverse effect of peroxide on activation polarization. The equation for $\frac{d\eta}{d \log i_{un}}$ similarly yields a limiting slope of -0.03 .

The point of minimum polarization on the curve of Figure 28 is 25 mv. and represents the polarization associated with all other factors when the peroxide concentration polarization is zero. If this value is subtracted from the ordinate value of each point in the curve of Figure 28 and the linear portion of the resultant curve extrapolated to zero polarization, the intercept yields a peroxide concentration of approximately 0.6 M. This value is assumed to be the concentration of peroxide existing at the interface of the particular electrode in 5 M KOH at 100 ma./cm.² The procedure used for obtaining this interface concentration is general.

The initial slopes at low current densities in Figures 21 and 25 provide an experimental check of the predictions of equation (57) which requires a tenfold

increase in the slope for each unit increase in the pH. The data indicate a rough correlation with the mean activity of the base. The higher limiting slope of the 10 M KOH is anomalous in this respect compared with the 5 M KOH in Figure 21. The anomaly is probably due to the resistivity effect discussed in the next section. In comparing the data of Figure 25 with theory it is necessary to assume that the Berl mechanism is applicable in acid solution.

The initial slopes at low current density in Figure 22 and 23 indicate smaller slopes for KOH which possess a higher activity than NaOH and LiOH and $(\text{CH}_3)_4\text{NOH}$ at equal molarities. For 5 M OH^- ion concentration, the mean activity coefficient of KOH is 1.7 times that of NaOH.

The predictions of equation (57) for the ratios of the initial slopes with the variable HO_2^- ion concentration (activity coefficient assumed constant) are approximately fulfilled in the data of Figure 26. Similar corroboration of equation (57) may be observed in the limiting slope of Figure 31 for varying oxygen pressure.

Quantitative checks of limiting slopes due to each reactant may be made only when the slope components due to other terms are small or eliminated by calculations based on concentration polarization theory.

The first term of equation (50) may be written as a combination of three terms where

$$62) \log \left(1 + \frac{k_2 I}{(a_{OH^-})} \right) \cong \log \frac{k_2 I}{(a_{OH^-})} \text{ for large } I$$

1.00,

$$63) \log \frac{k_2 I}{(a_{OH^-})} \cong + \log k_2 I - \log(M_{OH^-}) - \log(Y_{OH^-})$$

where (Y_{OH^-}) is the mean activity coefficient of the alkali.

When two different cations such as K^+ and Na^+ are compared, the difference in η predicted by equation (63) arises from the variation in the activity coefficients at the bulk alkaline concentration in question. The difference in the curves of 5 M NaOH and KOH should be a constant value according to equation (63) at high currents providing the other OH^- dependent terms are negligible. This difference is

$$64) \Delta\eta \cong 0.03 \log \frac{Y_{KOH}}{Y_{NaOH}}$$

In 5 molar alkali this is

$$65) \Delta\eta \cong 0.03 \log \frac{1.87}{1.096} = 7 \text{ mV}$$

The data of Figures (22) and (23) show slopes approaching the parallel state at high current densities, but the parallel distances are of the order of 25 mv. rather than 7 mv. for KOH and NaOH. K_2 has been assumed independent of the concentration of base for this discussion. A factor which has been neglected is that η will depend on the area of the electrode wetted by the respective base. Resistive effects described in section 2 which follows are also important.

If the last three terms are neglected, equation (50) predicts η at high current densities should be

Directly proportional to the log of the current and the curves of η vs I should resemble those of Figure 57a. Most curves are straight, however, because of the effect of terms involving the oxygen well as the resistivity effect described in the next section.

It is interesting to note that in regions where the last three terms of equation (50) may be neglected the slope is given by

$$6b) \quad \frac{\partial \eta}{\partial I} = \frac{.03}{I}$$

which is independent of the activities of any solutes. According to equation (56), at high current density the slopes are parallel and zero.

2. Resistivity Effect

Some features of the polarization associated with the oxygen electrode may be explained by the resistivity effect. Some of the pertinent phenomena which may be connected with this effect are listed below.

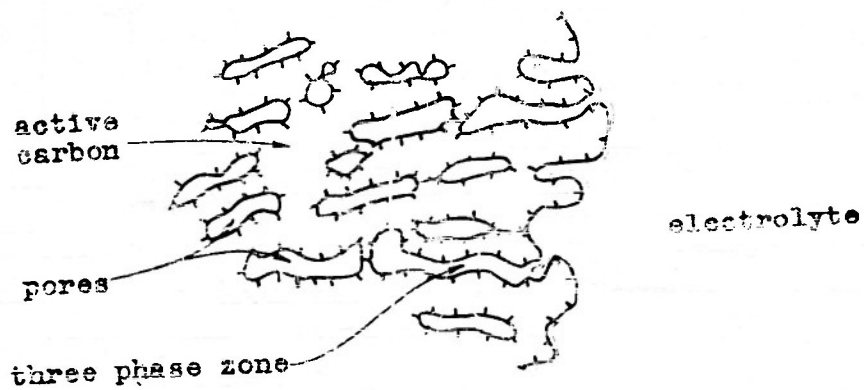
1. The polarization curves are linear at current densities above 50 ma./cm.²
2. The polarization seems to pass through a minimum value at or near the maximum conductivity of the solution.
3. The cathode decay traces are essentially flat at low currents but tend to decay considerably at higher current densities.

The first two of these three factors seem to indicate a resistive component in the polarization values. This, however, should not be the case since ordinary IR drop phenomena associated with polarization measurements are usually eliminated by the commutator technique for systems with uniform current density distribution. In the case of the carbon-oxygen cathode a somewhat unique situation exists. At low current densities sufficient active oxygen is present on the outer surface of the electrode to supply the needed depolarization. When the current is increased, this supply is exhausted and the electrolyte must penetrate into the carbon layer to obtain the oxygen required to support the current. Under these conditions a number of the small pores in the carbon become filled with the electrolyte. The following is a possible explanation of these phenomena.

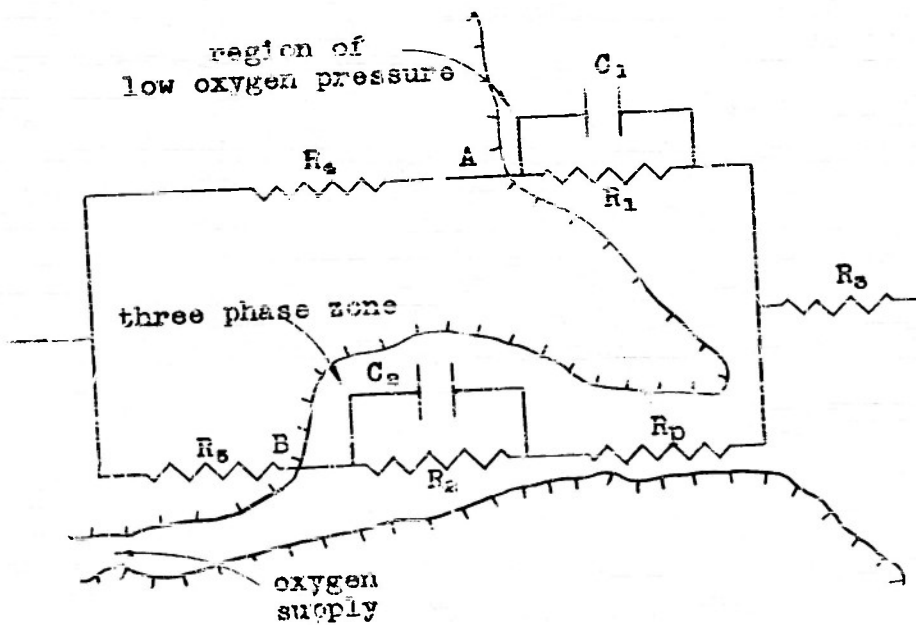
In Figure 39 is shown a greatly simplified diagram of the oxygen-carbon electrode and the situation that is postulated to exist at low and high current densities. Part 1 of this diagram above shows an idealized view of the electrode system, while part 2 shows an enlarged view of one pore with the equivalent electrical components superimposed. The phenomenon may be explained as follows.

If R_1 and R_2 are equal in the solid electrode, then points A and B are equipotential. R_3 represents the resistance of the bulk electrolyte which is eliminated from the measurements by the commutator. R_4 and C_1

I



II



Equivalent Electrical Analogue
in the Resistivity Effect

Figure 39

are the resistive and capacitive components associated with the electrode process occurring at or near the external surface of the electrode. R_2 and C_2 are the electrical components associated with polarization phenomena in the pores of the carbon and are of appreciable significance only at high current densities. R_p is the resistance of the solution contained in the pores and varies with the concentration and nature of the alkali.

At low current densities, the decay of the cathode trace is slight and the polarization is low. Under these conditions R_1 and C_1 function. As the current density is increased, the polarization at A rises due to the depletion of oxygen at the outer surface and the impedance of R_1 increases. At the same time the electrolyte begins to penetrate into the pore P due to electrocapillary action and reduced oxygen pressure and an appreciable current flows through R_2 and R_p .

In the idealized model the sum of the voltage drop across R_2 and R_p will be equal to that across R_1 providing R_2 and R_p are essentially equal. When the current is interrupted, the capacity of C_1 will discharge through R_2 and R_p as well as R_1 and the effect is to maintain the current through R_p for a short period of time after interruption. Since the polarization is measured within 1 microsec. after interruption, this condenser discharge will be included in the polarization values in the form of IR drop across R_p . There is reason to believe that the concentration and activation polar-

zation will show relatively small increments with increasing current density above 100 ma./cm.², and hence, the linear portions of the polarization curves will be due to the IR drop mentioned above. Since the resistance of R_p depends on the conductivity of the electrolyte, the pseudo polarization, i.e. IR drop, across R_p will exhibit a minimum at the maximum conductivity of the solution.

This same capacitive discharge through R_p will cause a rounding off of the cathodic decay curves. The effect becomes more significant at high current densities since R_1 becomes much larger.

The degree of flatness of the decay trace is ordinarily a measure of the degree of reversibility associated with the electrode process.²⁷ The electrode system may still be nearly reversible with respect to the electrochemical step even at high current densities although the cathode trace may decay considerably due to the effect just mentioned above.

The relative flattening of the decay trace of the cathode which has been observed with the catalyzed carbon electrodes compared to the non-catalyzed ones may be explained by this effect as follows. The extra liberated oxygen resulting from the decomposition of peroxide decreases the polarization associated with the external surface and the resistance R_1 decreases. As a

²⁷ D.C. Grabame, J. Phys. Chem., 57, 257 (1953).

consequence of this, less current flows through R_s and R_p and the total resistance of the discharge circuit for the condenser is less than before. This lower resistance discharges the condenser faster than before and the decay curve becomes flatter.

3. Activation Polarization

The concentration polarization associated with the active carbon-oxygen cathode has been shown to reach a minimum value by increasing the bulk concentration of perhydroxide ion. If the somewhat doubtful assumption is made that the concentration polarization is reduced to a negligible value by this procedure, then the residual polarization should be due to activation polarization and the resistivity effect. Figure 28 shows this residual polarization to be less than 25 mv. at a current density of 100 ma./cm.² When the data of Figure 29 are plotted on semilogarithmic axes, there is obtained a linear section (Figure 30) in the range from 5 to 50 ma./cm.² Since the length of this linear section is only one cycle, it is doubtful whether it represents a true Tafel curve. The slope of the linear section is only 0.01 which is smaller than the value expected from usual Tafel curves. Extrapolation of the linear section of Figure 30 to zero polarization gives an exchange current of 4 ma./cm.² which is indicative of a high degree of reversibility and a correspondingly low activation energy. It is reasonably evident that the exchange current is $>10^{-3}$ a./cm.².

The temperature coefficient of 0.5 mv./°C, mentioned earlier, is not a true activation polarization coefficient due to the temperature dependence of other types of polarization. In addition, the resistivity effect is also decreased by the increased conductivity of the electrolyte caused by the temperature increase.

The shape of the cathodic decay traces is closely related to the kinetics of the electrode process. The characteristics of cathodic decay traces have been previously discussed. For an electrode which has both activation and concentration polarization components, the rapid exponential decay may be due to the activation polarization, while the flatter slow decaying section may be caused by the concentration polarization. Since the resistivity effect likewise causes a rapid exponential fall of the decay traces, the separation of activation and resistivity effects by observation of cathodic decay traces may be difficult. The apparent decrease in the reversibility at high current densities as evidenced by the increasing decay rates has been discussed under the resistivity effect.

The Berl¹⁵ mechanism may be divided into several stages, any of which may be the slow process causing the activation polarization associated with the reduction of oxygen to peroxide in basic solution.

- a) The rate of sorption of oxygen.
- b) The transfer of a proton to the adsorbed oxygen
 - 1) From a hydrated ion,
 - 2) From a water molecule itself.
- c) The rate of desorption of the peroxide complex from the electrode site.

a. The rate of sorption of oxygen. --A mathematical treatment of the rate of oxygen sorption as the slow process assumes that the rate at which current flows is proportional to the rate at which oxygen molecules are sorbed on the sites. The electrochemical potential is proportional to the logarithm of the ratio of the covered sites to the uncovered sites.

Thus it follows that

$$E_{rev} = E^0 - \frac{RT}{nF} \ln \frac{n_{rev}}{N - n_{rev}}$$

where E^0 is a constant for the electrode, n_{rev} is the number of sites occupied under reversible conditions, and N is the total number of sites available. It is assumed that the oxygen complex stands up on and from the site and that adsorption on one site does not influence the potential energy of neighboring sites. If the oxygen is adsorbed in such a fashion that two

neighboring sites are required, the ratio is raised to the power of two in equation (67). Under dynamic conditions, in a steady state, the number of sites which have adsorbed oxygen is n , and

$$(68) \quad E_H = E^0 - \frac{RT}{nF} \ln \frac{n}{N-n}$$

The net current I is related to the sorption process by the equation

$$(69) \quad I = (c_{O_2}) (F_{O_2}) (N-n) - k_2 (n),$$

where k_1 and k_2 are constants. Combination of (67), (68), and (69) yields

$$(70) \quad \eta = A - \frac{RT}{2F} \ln \frac{k_1 (k_1 PN - I)}{k_1 P (Nk_2 - I)}$$

If the fraction of the sites occupied is assumed to be small, equation (70) simplifies to

$$(71) \quad \eta = A - \frac{RT}{2F} \ln \frac{k_1 PN - I}{k_1 PN}$$

When n approaches N , the term $(Nk_2 - I)$ approaches zero in equation (70) and the polarization goes to infinity.

b. Transfer of protons. --It is possible that the transfer of a proton from a hydrated ion or from a water molecule itself could be the slow process causing the activation polarization. The transfer of a proton from a water molecule involves about 5 to 10 kcal. of energy. The abstraction of a proton from a hydrated ion requires less than this amount. The ease with which a proton is removed from a hydrated positive ion is dependent on the charge of the ion, the radius of the ion, and the number of water molecules in the hydrated atmosphere. The differences in polarization which have been observed between LiOH, NaOH, and KOH are quite small. $(\text{CH}_3)_4\text{NOH}$

has a considerably higher polarization, however, than the alkali metal hydroxides for the same concentrations of base. This base has a smaller potential energy of interaction between the water molecules and the positive ion than the others mentioned above.

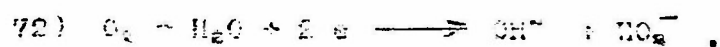
c. Desorption of the peroxide complex. --The rate at which the perhydroxide complex desorbs from the surface is dependent on the stability of the adsorbed complex. This stability is a function of the degree of hydration of the complex, the concentration of alkali in the vicinity of the site, and the electric field. The rate of desorption of the complex is probably exponentially proportional to the polarization.

In conclusion, the amount of activation energy associated with the electrochemical reduction of oxygen to peroxide at highly activated carbon electrodes in basic solution is quite small. The large number of other factors obscure the true activation polarization so that a quantitative evaluation is not possible with the available data.

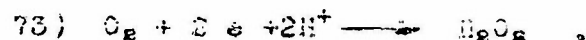
F. The Oxygen Electrode in Acid and Neutral Solution

A combination of data from static measurements in basic solution with static potentials obtained during polarization measurements in neutral and acid media are shown in Figure 40. This figure shows that the slope of dE/dpH at constant peroxide concentration and oxygen partial pressure changes from 0.03 to 0.05 below pH 7.

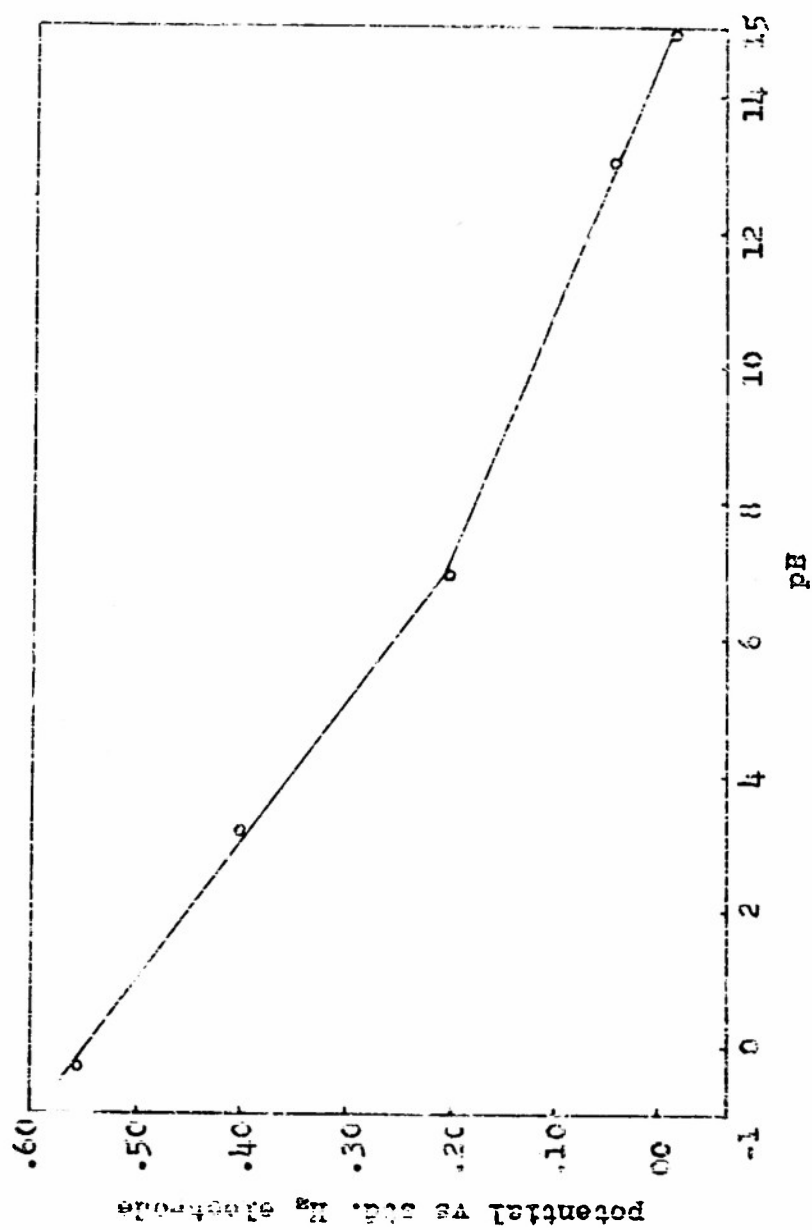
From the equation for the reduction of oxygen to peroxide in basic solution



one obtains in acid solution by the addition of two hydrogen ions to each side of the reaction



The Nernst equation for this half cell reaction is



Potential vs pH Curve

Figure 10

$$74) E = E^{\circ} - 0.059 \log \frac{(a_{H_2O_2})^{1/2}}{(a_{H^+})(a_{O_2})^{1/2}}$$

which should give a slope of -0.059 for dE/dpH , $+0.03$ for $dE/d\log a_{H_2O_2}$, and -0.03 for $dE/d\log a_{O_2}$. The experimental slope in acid solution is -0.05 for dE/dpH as previously stated; the other factors remain to be confirmed.

Kondasch and Martinola¹⁶ report that the static potentials of the oxygen electrode exhibit sluggish or zero response to changes in the oxygen partial pressure at pH values below 9. The results are subject to some doubt since no peroxide control was maintained. Other workers have intimated that the dynamic oxygen electrode departs from reversible behavior at low pH.

Causes of insensitivity to variable oxygen pressure may be the predominance of electrode reactions and of mechanisms other than that of H_2O_2 ¹⁶. For example, the Bratzler¹⁸ mechanism involving the depolarization of adsorbed nascent hydrogen by oxygen may be responsible for the majority of the electrode processes. The desorption of nascent hydrogen from the site by a chemical reaction with oxygen may be rapid compared with the rate of the electrochemical reaction of formation of nascent hydrogen. Increased activity of oxygen under such circumstances could effect only minor changes in the potential.

A possible explanation for the behavior of the oxygen cathode in neutral and acid media may be deduced from the work of Winslow²⁸ on the sorption of acids by active carbons and the oxidizing power of these carbons in the presence of oxygen. This author postulated the active oxygen as being present in the form of a peracidic rather than peroxidic complex. This was evidenced by the fact that the complex would not reduce permanganate as would a peroxide like structure.

If the active oxygen were present in the form of this peracidic complex at the oxygen cathode in acid solution, the stability of this form would be greater than the normal physically adsorbed oxygen and a higher activation energy would be required for its reduction.

The changes in the behavior of the electrode with decreasing pH would be explained by the amount of oxygen which would be present in the peracidic complex as compared to the physically adsorbed material. At high acid concentrations practically all the oxygen present on the carbon would be in the peracidic form.

G. Future Work

A few suggestions for future work on the oxygen electrode will be made under the following classifications:

²⁸ N.M. Winslow, Trans. Electrochem. Soc., 92, 411 (1947).

- 1) Static measurements
- 2) Dynamic measurements
- 3) Isotopic tracer studies

1. Static Measurements

A series of static measurements in which the potentials of active carbon and catalyzed active carbon electrodes are studied as functions of oxygen partial pressure and peroxide concentration at pH values below 7, would be of value in determining the mechanism of these electrodes in acid media.

2. Dynamic Measurements

A great variety of work remains to be done with dynamic measurements on the oxygen electrode.

a. A quantitative relationship between surface area and polarization would be valuable.

b. The difference between the amount of oxygen adsorbed by a carbon and the quantity available for electrochemical reduction should be measured.

c. The effect of decreased activity of water might be more clearly shown by using an inert material such as diatomite to reduce the activity of water in the electrolytes.

d. The effects of varying oxygen partial pressure and temperature should be studied to determine

the amount of activation polarization present.

f. A mathematical theory of the resistivity effect should be formulated which will permit a quantitative treatment of this factor.

3. Isotopic Tracer Studies

A study of the oxygen electrode using oxygen enriched with O^{18} as the depolarizing material would be useful in studying the kinetics of this electrode.

BIBLIOGRAPHY

- Adler, H., "Accounts of Experiments with
Immersed in Pure Water and O₂
Phil. Mag. 31, 310 (1947).
- Bain, H.G., "Neutralized Glass Oxygen in
Microscopic. Soc., 75, 173
- Bart, W.G., "Reactions of Peroxide and
Hydrogen Peroxide" Trans. 1947
- Bart, H., "New Cathodic Process for
Electrodeposition. Soc.
- "Formation and Properties
of Iron" Trans. Soc.
- Bart, H.G., "Reversible Oxygen Electrode
Electrochem. Soc., 1943
- Bart, H.G., "The Electrodeposition of
Iron" Trans. Soc., 39,
- Bartman, "The Electrodeposition of Iron" Knapp,
1947.
- Bartman, H., "The Electrodeposition of Iron
and the Electrodeposition of Iron" Soc.
- Bartman, H. and Bartman, H., "The Use of
the Electrodeposition of Iron" Soc.
- Churchill, J.B., "The Electrodeposition of Iron
and the Electrodeposition of Iron" Soc.
- Danavaz, "The Electrodeposition of Iron" Soc.
- Fischer, F. and Fischer, F., "The Electrodeposition of Iron
and the Electrodeposition of Iron" Soc.

BEST AVAILABLE COPY

UNCLASSIFIED

UNCLASSIFIED